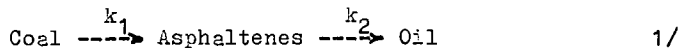


ASPHALTENES AND PREASPHALTENES - COMPONENTS OF AN ORIGINAL hvb COAL

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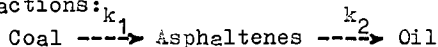
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Asphaltenes are considered to be the principle intermediates in the conversion of coal to an oil products. Weller /1/ stated that the catalytic conversion of coal involves two consecutive first order reactions:



At 400°C k_1 was reported as 27 times higher than k_2 and at 440°C k_1 as 10 times higher than k_2 .

Liebenberg and Potgleter /2/ derived another mechanism which includes the following reactions:



He tentatively determined the sum k_1+k_2 at 400°C and 440°C in the conversion of coal with tetralin and no catalyst added.

More recently Yoshida et al. /3/ established that the mechanism for catalytic conversion of Hokkaido coals includes Reaction 1 and 3. It is worth to emphasize that according to their experiments k_4 is considerably higher or lower than k_1 and k_2 , depending upon coal type.

Sternberg et al. /4,5/ have proposed that preasphaltenes are the intermediates between coal and asphaltenes. Contrary to this, Schwager and Yen /6/ considered that "preasphaltenes may arise from reactive coal depolymerization moieties, which are ... repolymerized into materials more difficult to degrade than the original coal substance".

Collins et al. /7/ claim that "carbon-carbon scission must be considered as an important factor in asphaltene formation" and in preasphaltenes formation as well. The statement has arisen from their experiments based on thermal treatment /over 300°C/ of model compounds - arylalkanes, diphenylalkanes and aryl alkyl ethers.

We have found that asphaltenes and preasphaltenes are the components of coal extracts. Coals were extracted at ambient temperature and precautions in analytical procedure have been observed. Therefore, the components of the extract may be considered they are the components of original coal.

EXPERIMENTAL

High volatile A bituminous coal J /vitrinite 60%, inertinite 33%, exinite 6%/ and hvab coal W /vitrinite 45%, inertinite 45%, exinite 10%/ have been investigated. Proximate and ultimate analyses are presented /Table 1/.

EXTRACTION

Coal samples / <1,4mm/ were extracted in the Soxhlets at ambient temperature for 150 hours. Benzene-ethanol 7:3 vv mixture has been applied. Yields and ultimate analysis of the extracts are given /Table 1/. Although the yields are low they are considerably higher than benzen extract or ethanol extract yields.

Temperature curriculum of the extracted compounds: after extraction at ambient temperature the extract solution has been influenced by temperature below 100°C /the bottom flask of the Soxhlet water bath heated/ for 18 hours /after each 18-hour period, solution has been removed and fresh solvents poured/. The total extract solution was carefully filtrated and the solvents were evaporated from it in a rotary apparatus at 50°C and reduced pressure.

FRACTIONATION OF THE EXTRACTS

has been carried out according to the scheme /Fig. 1/ based on the procedure described by Schweighardt et al./8, 9/ for analysis of hydrogenated coal liquids.

The following group components have been isolated /Table 2/:
preasphaltenes i.e., benzene insolubles/pyridine solubles
asphaltenes i.e., benzene solubles/hexane insolubles
basic fraction of asphaltenes
acidic/neutral fraction of asphaltenes
benzene and hexane solubles

Temperature curriculum of the extracted compounds, continued: all group components were freed from the solvents in a rotary apparatus at 50°C /except pyridine insolubles/ and reduced pressure to constant weight /except pyridine solubles/. Other analytical works were done at ambient temperature. Samples were stored in nitrogen.

Extract+benzene /10g:100ml/ were vigorously stirred for 3 hours. Benzene insolubles BI were filtrated, washed, dried, weighed. Then pyridine was added to BI and total - stirred for 1 hour. Pyridine insolubles PI were filtrated, washed and dried above 100°C to constant weight.

The content of pyridine solubles PS has been determined by difference:

BI - PI = preasphaltenes,
since some final amount of pyridine cannot be removed from them at 50°C.

Solubility of preasphaltenes

We tried to redissolve the preasphaltenes in the same solvent mixture as applied in coal extraction /benzene:ethanol 7:3/. It has been stated that preasphaltenes isolated from the coal extract are easily dissolved at ambient temperature in the mixture, although they are insoluble in benzene or ethanol. Therefore, no indication of their polymerization /6/ which could contribute to a formation of preasphaltenes has been found.

Further analytical work on the separation of preasphaltenes by HCl saturation of benzene/ethanol solution has not been completed yet.

The benzene soluble portion of the extract is reduced in volume by nitrogen flush at 50°C until an approximate ratio 1g:5ml solubles: benzene is reached. Then BS concentrate is slowly introduced by drops into vigorously stirred hexane. Filtrated, washed and dried precipitate yields the content of asphaltenes.

The asphaltenes are dissolved in toluene, filtrated, then dry HCl is bubbled through the solution until no further precipitation is observed. Chloride precipitate is freed from HCl by toluene/1n aqueous NaOH treatment and after evaporation of toluene the content of basic portion of asphaltenes is determined. Compounds which did not form HCl adducts and remained in toluene were recovered by evaporation /nonbasic portion of asphaltenes/.

TLC ANALYSIS OF THE EXTRACT AND ITS SEPARATION PRODUCTS

Table 3. Thin-Layer Chromatography conditions

	Solvent system			Solvent ratio			Development cycle
	M	C	B	M	C	B	
extract	methanol	chloroform	--	1 : 1	-	-	1/2; full
preasph.	methanol	chloroform	benzene	1 : 1	: 1	-	full
bases	methanol	chloroform	--	1 : 1	-	-	full
nonbases	methanol	chloroform	--	1 : 1	-	-	1/2; full

Neutral gel /type MN-Kieselgel HF/ on 20x20 cm plates was used. Full development cycle was 16 cm high; 1/2 cycle is realized as follows; the plate is kept in the chamber until solvent reached 1/2 height, removed from chamber, dried under nitrogen, reinserted in chamber.

The applied spray reagents for functional group detection on TLC plates are presented /Table 4/.

Table 4. Thin-Layer Spray Reagents

Reagent	Functional group indication			Ar-NH ₂ Amines	Detection limit / g/
	Ar-OH Phenol type	N-H ring Pyrrol type	=N-ring Pyridine type		
Fast Blue Salt B	red- violet	brown- violet	--	yellow- orange	0,01
FeCl ₃ 3% in 0,5n HCl	violet	dark green	--	blue	0,01
Wachmeister's Reagent	yellow- violet	purple- brown	--	brown- green	0,1
Erlich's Reagent	--	violet ^a	light yellow	light yellow	0,05
Dragendorff's Reagent	--	--	orange	pink- red	0,1
Iodoplatinate	--	--	brown	beige	0,5

^a/after few hours

Preparation of the reagents is based on E. Merck handbook - "Anfärbereagenzien für Dünnschicht- und Papier-Chromatographie", Darmstadt, 1970. The same reagents were applied by us /10/ in analysis of hydrogenated coal liquids.

Results of TLC analysis of the coal extract as well as its separation products are summarized /Table 5/.

Table 5. Results of Spray Reagent Test:

	Ar-OH Phenol type	N-H ring Pyrrol type	Functional Group =N- ring Pyridine type	Ar-NH ^a Amine ²
Extract	+	+	+	+
Preasphaltenes	+	+	+	+
Asphaltene bases	---	---	+	+
Asphaltene acidic/neutral	+	+	---	---

a/ TLC-Spray Reagent indication of amine presence is not an irrefutable proof.

b/ Meaningless test - preasphaltenes are contaminated by pyridine during separation procedure.

The results indicate that asphaltenes derived from the coal extract contain heterocompounds which may be separated into basic and acidic/neutral fractions. Phenol and pyrrol derivatives are present in the acidic fraction, pyridine derivatives -- in the basic portion. We did not find any amphoteric substances in the basic nor in the acidic fraction. Therefore, the analogous results have been obtained in analysis of asphaltenes extracted from coal at ambient temperature /this paper/ and asphaltenes derived from the high temperature coal conversion products /5, 8, 9, 10/.

INFRA-RED SPECTROMETRY OF THE EXTRACT AND SOME SEPARATION PRODUCTS

Spectra have been recorded by C. Zeiss spectrophotometer Specord 71 IR Model /NaCl prism/.

Spectra of the extract in KBr pellet /curve A/, basic fraction /curve B/ and acidic/neutral fraction of asphaltenes /curve C/ - both in 2% CS₂ solutions, 0,6 mm fixed path length cell, are presented /Fig. 2/. CS₂ bands have been compensated by application of variable path cell² in reference beam.

Broad and high band in 3590-3050 cm⁻¹ range is a strong indication of the presence of hydrogen bonded heterocompounds in the extract.

Spectrum of bases shows:

in 3570-3100 cm⁻¹ range - weak, broad band which may arise from stretching vibrations of N-H group, free or/and hydrogen bonded; taking into account TLC-spray reagent test results /pyrrol type N-H and phenol type O-H excluded/ the above band arise from amine type N-H bond.

1730 cm^{-1} band indicates carbonyl group of cyclic unsaturated ketones, and/or diketones, and/or quinones. However, this band is absent in the extract spectrum. Therefore, oxidation of the basic fraction may be a reason.

Spectrum of acidic/neutral fraction shows:

in 3585-3550 cm^{-1} range - sharp band characteristic of free phenol O-H and/or intramolecular phenol O-H..... π orbital band;

in 3495-3100 cm^{-1} range - broad band characteristic of intermolecular O-H bonded group; absorption of pyrrol type N-H stretching and/or NH...OH vibrations occurs within the range as well;

sharp 1030 cm^{-1} band may arise from symmetric stretching vibrations of C-O-C aryl ethers and/or skeletal vibrations of furanes; the presence of furanes is indicated as well by 880 and 860 cm^{-1} dublet.

However, the assignment of all other bands has been carried out, it is not presented here, since complex composition of the samples limits its diagnostic value. On the other hand, part of it is clearly visible and trivial, for instance - higher content of aromatic and alkyl groups in acidic fraction than in basic fraction.

CONCLUSIONS

Asphaltenes and preasphaltenes are the components of an original coal. Therefore, some portions of these group components in coal liquefaction products are not the products of thermal nor catalytic conversion.

The real content of asphaltenes and preasphaltenes in an original coal is still an unanswered question. We have yet to know more on electron-donor and -acceptor properties of solvent mixtures as well as about strength of donor-acceptor bonds occurring in coal substance, if one intends to select solvent mixture capable of extracting total amount of these components from coal.

ACKNOWLEDGEMENT

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TABLE 1. Proximate and ultimate analyses of the coals^{a/}
yields and ultimate analysis of the extracts

	Mad	Ash ^{ad}	V ^{daf}	C	H	N	S	O ^{b/}	Yield ^{c/}
Coal J	4,34	4,02	39,05	82,34	5,40	1,64	0,57	10,05	-
Extract from "	-	-	-	82,43	7,45	1,00	0,64	8,48	4,51
Coal W	4,90	9,00	37,40	80,67	5,11	1,40	0,87	11,95	-
Extract from "	-	-	-	82,65	7,08	1,15	1,55	7,57	4,47

a/ Ultimate analysis is given in wt % of daf coal

b/ By difference

c/ Yields of extract are given in wt % of daf coal

TABLE 2. Group composition of coal extracts

Group Composition	Content of the components in /wt %/ :				
	Extract from Coal J	Coal J ^{a/}	Extract from Coal W	Coal W ^{a/}	
Pyridine insolubles /PI/	1,1	0,04	1,0	0,04	
Treaspthaltenes /PS/	45,3	2,04	42,7	1,91	
Asphaltene /HI/	23,4	1,06	27,5	1,23	
Bases	4,8	0,22	6,7	0,30	
Acids + neutral cpds	18,6	0,84	20,8	0,93	
Hexane solubles /HS/	22,5	1,02	24,2	1,08	
Lost	7,7	0,35	4,6	0,21	
TOTAL	100,0	4,51	100,0	4,47	

a/ Data are given in weight percent of daf coal

FIG. 4.

EXTRACT FRACTIONATION SCHEME

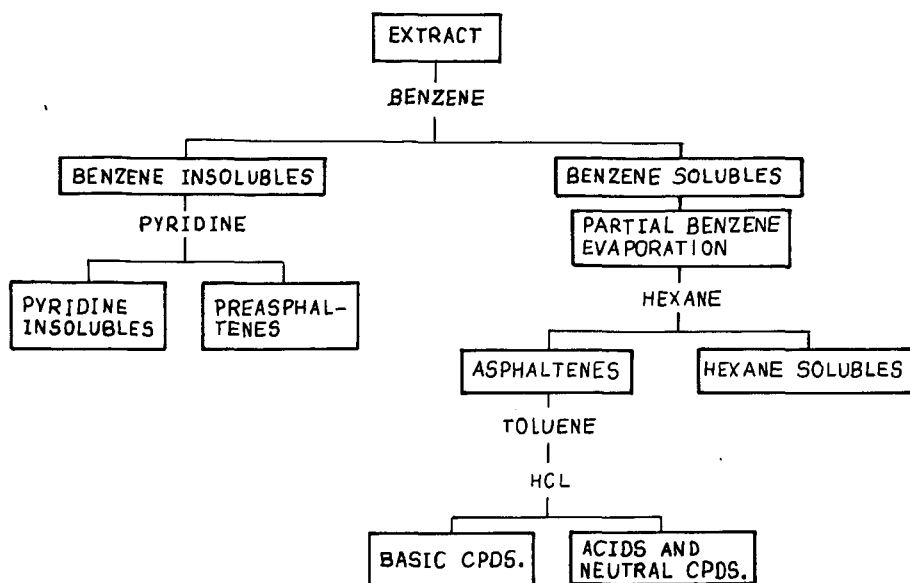
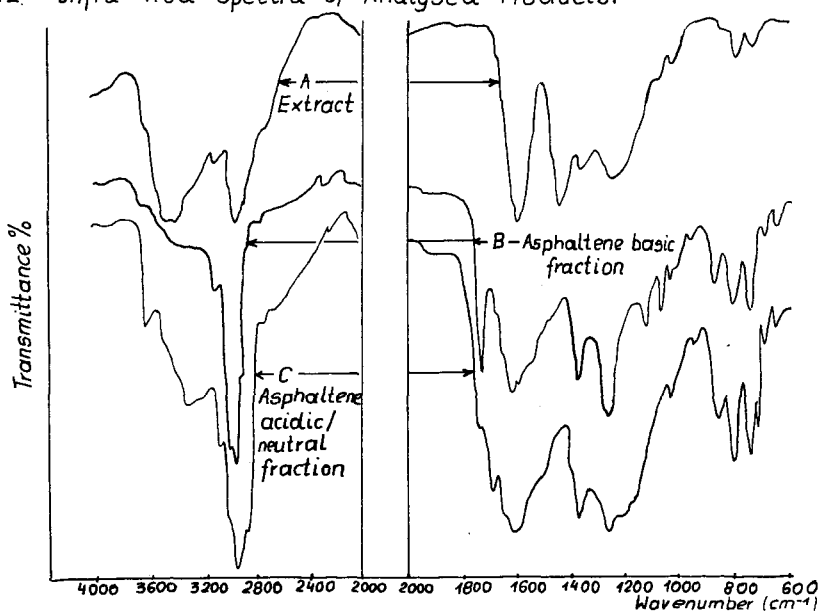


Fig.2 Infra - Red - Spectra of Analysed Products.



THE HYDROTREATMENT OF COAL WITH AlCl_3/HCl AND OTHER
STRONG ACID MEDIA

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INTRODUCTION

Most current processes for upgrading coal to cleaner fuels require stringent reaction conditions of high temperatures and pressures. Less severe reaction conditions are needed to make coal upgrading economically feasible. The objective of this work was to investigate catalyst systems for upgrading of coal to clean fuels under moderated conditions. In this work, homogeneous acid catalysts are of particular interest because they allow intimate contact with the coal, they are not liable to coal ash fouling, and they are easily recovered from the coal ash.

The most common homogeneous catalysts studied in coal upgrading belong to the general class of molten salt catalysts, (1-5) and include halide salts of antimony, bismuth, aluminum, and many of the transition metals. Most often, these molten salts have been studied at high temperature, and in massive excess. (1-5) We have performed a systematic study of the use of some of these molten salts as the homogeneous acid catalysts for upgrading of coal at relatively low temperatures and moderate quantities.

In our initial work to establish relatively mild reaction conditions that would still give relatively good conversions, we conducted a series of experiments to determine the role of HCl , AlCl_3 , and H_2 in coal hydrocracking. We examined the effects of temperature and residence time, studied catalyst/coal weight ratios of 1:1 to 3:1, and finally chose the standard reaction conditions for the screening of several acid catalysts. This paper summarizes the experimental studies and our results.

EXPERIMENTAL STUDIES

We used Illinois No. 6 coal, which was pulverized by ball milling under nitrogen to 60 mesh and then usually dried in a vacuum oven at 115°C overnight. Pennsylvania State University supplied beneficiated coal samples (PSOC-26) as well as an unbene-ficiated sample (PSOC-25) for use in some experiments. The reactor used was either a rocking 500-ml autoclave fully lined with Teflon, or a 300-ml Hastelloy C Magne-Drive stirred autoclave from Autoclave Engineers. Standard tetrahydrofuran (THF) and pyridine solubilities were determined for the dried product coal by stirring a 0.50 g sample of the product coal in 50 ml THF or pyridine at room temperature for 1 hr, filtering the mixture in a medium porosity sintered glass filter, and then washing the residue with fresh solvent (~ 50 ml) until the washings were clear.

RESULTS AND DISCUSSION

In a series of runs in a rocking Teflon-lined autoclave, we first studied the role of HCl , AlCl_3 , and H_2 in coal hydrocracking, using 5 g each of AlCl_3 and coal, at 190°C (just above the melting point of AlCl_3), for 15 and 5 hr. As shown in Figure 1, one or more of the three components were absent in Runs 1 to 6 and 9, and in each case no increase in THF and pyridine solubilities was observed. In Run 10, where all three components were present, solubilities increased substantially, suggesting that the AlCl_3/HCl system was active. Runs 7 and 10 serve to assess the importance of HCl in the system under these conditions, however the results are not unequivocal. Here, the presence in the coal of proton sources, such as phenolic groups and traces of water, undoubtedly hydrolyzes some of the AlCl_3 , producing HCl .

These runs indicate that no added HCl is required for coal hydrocracking at these lower temperatures.

At higher reaction temperatures (210°C) and shorter reaction time (5 hr) on the other hand, the added HCl clearly increases the conversion (Runs 21 and 25), suggesting that the effective catalyst in the system must contain the elements of HCl and AlCl_3 .

Next, we studied the effect of potential H-donor hydrocarbons and temperature. We based our work on the results of Siskin, (5) who found that saturated, tertiary hydrocarbons serve as effective hydride donors in the strong acid-promoted hydrogenolysis of benzene. In our system they proved ineffective (Runs 17, 22, 24, and 26, Figure 1). Higher temperatures allowed shorter reaction times. The results for Run 18 (only 5 hr at 195°C) are comparable to those for Runs 7 and 10 (15 hr, 190°C). Runs at 195°C for 15 hr were significantly more effective, and the conversion for Run 12 at 5 hr and 210°C is about the same as that of Run 16 for 15 hr at 195°C.

Next, we studied the effects of the reaction period and catalyst to coal weight ratio on both the product character and the coal product yields in both the Teflon-lined and the Hastelloy C autoclaves. We first compared the effects of the catalyst/coal ratio and at a weight ratio of 1.0, the two systems yielded products with strikingly different pyridine solubilities: about 60% with the Teflon equipment. Increasing the catalyst/coal ratio to 2.0 increased solubilities to above 90%, but a further ratio increase actually caused solubilities to decrease slightly. The solid product recovery also decreased with increasing catalyst/coal ratio. At a 2.0 ratio, only about half the coal was recovered as a solid product. The other half was gasified. The softening point for the THF-soluble fraction was about 150°C; however, the pyridine-soluble fraction did not melt even up to 280°C. The coal products from the Teflon-lined reactor have consistently higher H/C ratio than those from the Hastelloy C reactor. We have no detailed explanation for the effect of autoclave surface on the results, but passivation of the metal surface by some minimum quantity of catalyst is part of the answer. Whatever the mechanism, the Teflon surface is helpful.

In runs over varying residence times in the Hastelloy C autoclave at a constant 2.0 catalyst/coal ratio, we observe significant differences in gasification. In runs of 5 hr down to 90 min, solid product recovery was 45 to 50%. In the 45 min runs, solid product recoveries were 66 to 72%. The H/C values for the isolated solid product coals for all six runs were remarkably similar, from 0.82 to 0.85. Similarly, all coal products have pyridine solubilities greater than 90%. The following scheme may explain these data.

The catalyst system gasifies some of the coal directly to methane and ethane. This result, and the effects of temperature on coal conversion, are shown in Table 1.

The Table shows data from runs at 210°C for reaction times from 45 min to 5 hr, and at 300°C for experiments all for 90 min. (the 210°C data are from an earlier phase of our work, where the gasification was not quantified. Thus the gasification was determined by difference. For the 300°C work, the quantities of gases and residue were determined independently, and thus the mass balances for these runs are not exactly 100%).

From the lower temperature results, it is seen that the degree of gasification increases with increasing reaction time. The solid coal products from these runs are all highly pyridine soluble, and have effectively the same H/C ratio, of 0.83 - 0.84. (The H/C ratio of the starting coal is 0.79).

The 300°C runs are all for 90 min, and experiments 83 and 85 show striking degrees of gasification. Fully 90+% of the carbon in the coal was converted to a

50:50 mixture of methane and ethane in these experiments. The next three runs were run without HCl present, and a cumulative effect of its absence is seen. The degrees of gasification decline severely, and the solid coal products recovered all have lessened pyridine solubilities and H/C ratios. A similar effect for HCl was observed by Kawa, et al.(2).

These data can be explained by the following scheme.

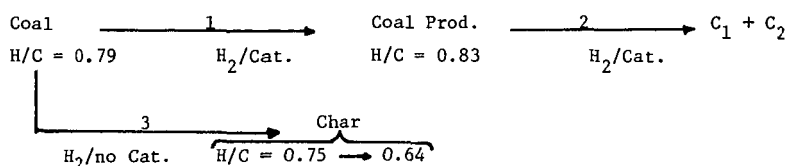


Table 1

THE EFFECT OF RESIDENCE TIMES ON COAL GASIFICATION

(4 g Illinois No. 6 coal, 8 g AlCl_3 , 500 psi HCl, 800 psi H_2 , in a 300 ml stirred Hastelloy C autoclave)

Run	Residence Time	Coal Residue			% Coal Gasified	
		% Rcvd	% Pyr Sol	H/C		
210°C						
67	5 hr	39	97	0.83	61 ^b	
46 ^c	"	48	87	0.82	52 ^b	
41	4 hr	49	91	0.84	51 ^b	
66	90 min	47	96	0.85	53 ^b	
69 ^d	45 min	72	93	0.82	28 ^b	
71	"	66	97	0.84	34 ^b	
300°C						
Run Without HCl	83	90 min	18	78	0.72	96
	85	"	18	83	0.74	90
	86	"	30	60	0.75	72
	87	"	49	31	0.68	56
	88	"	68	28	0.64	36

^aBased on 4 g of coal.

^bAssumed, based on unaccounted for material.

^cRun with 3 g coal and 6 g AlCl_3 .

Steps 1 and 2 are important in the presence of an effective catalyst and 3 becomes competitive with no effective catalyst present. At lower temperatures, $k_1 > k_2$. Thus, the hydrogen-rich, pyridine-soluble coal product accumulates and can be isolated. At high temperatures, the relative rates of Steps 1 and 2 are reversed, $k_2 > k_1$, and gasification is the major effect. Finally, when the elimination of HCl reduces the catalyst effectiveness, Steps 1 and 2 are suppressed and 3 becomes dominant. Thus

AlCl_3 alone is not only ineffective, it promotes char formation.* Moreover, with the lessening degrees of gasification, the coal residues appear to be increasingly cross-linked and depleted in hydrogen, possibly a result of chemistry at the autoclave surface.

Several acid catalysts were screened in two series of tests at two catalyst concentration levels, 210°C, 5 hr, 800 psi H_2 , and 0.7 M HX (X = Br, Cl, or F). We found catalyst activity to vary considerably from one series to the next (Table 2). Catalyst coal ratio for the first series was 1:1. All catalysts studied at this ratio, except AlBr_3 and AlCl_3 , were ineffective, reducing THF and pyridine solubilities significantly, perhaps because of internal condensation in the starting coal. The coal products in these runs are probably highly cross-linked. AlCl_3 was considerably more effective than AlBr_3 , and HBr alone (Run 30) was, not surprisingly, ineffective. We found HCl to behave similarly (Run 4, Figure 1). Thus, these results indicate a catalyst effectiveness of $\text{AlCl}_3 > \text{AlBr}_3 > \text{SbCl}_3 \approx \text{SbF}_3 \approx \text{ZnCl}_2 \approx \text{TaF}_5 \approx \text{NiSO}_4 \approx \text{CoSO}_4 \approx \text{HBr}$.

Next we ran a more extensive series with the catalysts present at a constant ratio of 0.045 M catalyst/4 g coal, equivalent to 6 g AlCl_3 /4 g coal. Here we found $\text{SbBr}_3 \approx \text{SbCl}_3 > \text{AlBr}_3 > \text{AlCl}_3 > \text{Ni}(\text{AA})_2 > \text{TaF}_5 >> \text{SbF}_5 \approx \text{MoCl}_5 \approx \text{WCl}_6$ (AA = acetylacetonate). In this second series we found first that TaF_5 , which Siskin (6) found to effectively hydrocrack benzene to mixed hexanes, is not at all effective under our conditions. Similarly, ZnCl_2 , the well known coal conversion catalyst, is not effective under these conditions, perhaps because under our relatively mild conditions, ZnCl_2 is not molten (mp, 283°C). Finally, the favorable antimony bromide and chloride results are similar to those reported by Shell (1).

In Run 35 (Table 2), with AlCl_3/HCl , we used unbeneficiated coal. Here, the THF solubility of the product coal increased by almost a factor of 2, to 40%. The pyridine solubility increased slightly, to 66%. Since pyridine is generally a better solvent for coal liquids than is THF, the considerable increase in THF solubility suggests that more lower molecular weight products are obtained when unbeneficiated coal is used. Also, the mineral matter present in the unbeneficiated coal clearly aids in the acid-catalyzed hydrocracking process, suggesting that the mineral matter in the coal is an effective catalyst under acid conditions.

SUMMARY OF RESULTS

We now have established a set of relatively mild experimental conditions for coal conversion and have identified several homogeneous acid catalysts, which under these conditions can convert the coal almost completely to pyridine-soluble material. The reaction conditions for AlCl_3 are 210°C, 45 min, 2:1 AlCl_3 /coal weight ratio, 500 psi H_2 , 800 psi HCl. Also, we have observed that with 1:1 catalyst/coal weight ratio, the effectiveness of the catalysts for conversion is

$\text{AlCl}_3 > \text{AlBr}_3 >> \text{SbCl}_3 \approx \text{SbF}_3 \approx \text{ZnCl}_2 \approx \text{TaF}_5 \approx \text{NiSO}_4 \approx \text{CoSO}_4$.
When a constant molar ratio of catalyst is used, the order is:

$\text{SbBr}_3 \approx \text{SbCl}_3 > \text{AlBr}_3 > \text{AlCl}_3 > \text{Ni}(\text{AA})_2 > \text{TaF}_5 >> \text{SbF}_5 \approx \text{MoCl}_5 \approx \text{WCl}_6$.

We have discovered that adding HCl to AlCl_3 significantly enhances conversion for runs with short residence time (5 hr or shorter) at 210°C. Under similar reaction conditions, a Teflon-lined reactor yields coal products with greater H/C values than does the Hastelloy C reactor. Residence time also has a significant effect on gasification. More than 50% of the coal is gasified for residence times of 95 min or longer; 30% is gasified at 45 min. Finally, we have established that at 300°C reaction temperature, AlCl_3 /coal weight ratio of 2:1, and with HCl added, about 90% of the coal is converted to methane and ethane.

*The cumulative effect of HCl absence is explained by the need for passivated reactor surfaces. When these reactions are run in fully Teflon-lined reactors, the results are significantly improved. Considerably lower catalyst/coal ratios provide results comparable to those shown here.

Table 2
TREATMENT OF ILLINOIS NO. 6 COAL
WITH H₂/STRONG ACID SYSTEMS

Run #	Catalyst System	Pressure (psi)		Solubilities (%) ^b	
		H ₂	HX	THF	Pyr
(a) <u>Constant Weight</u> ^a					
28	AlCl ₃ /HCl/H ₂	800	500	23	58
35	AlCl ₃ /HCl/H ₂ ^c	800	500	40	66
29	AlBr ₃ /HBr/H ₂	980	33g	9	27
27	AlBr ₃ /HBr/H ₂	820	50g	11	32
30	HBr/H ₂	1000	31g	2	6
31	SbCl ₃ /HCl/H ₂	800	500	-	1
32	TaF ₅ /HF/H ₂	1100	22g	-	13
33	SbF ₃ /HF/H ₂	1100	16g	< 1	4
44	ZnCl ₂ /HCl/H ₂	800	500	-	9
56	CoSO ₄ /H ₂ SO ₄	1300	68.6g	< 1	< 1
57	NiSO ₄ /H ₂ SO ₄	1300	68.6g	< 1	< 1
(b) <u>Constant Molar Quantity</u> ^d					
45	AlCl ₃ /HCl/H ₂	800	500	25	47
48	AlBr ₃ /HBr/H ₂	1100	70g	30	59
49	SbCl ₃ /HCl/H ₂	800	500	-	~100
50	TaF ₅ /HF/H ₂	900	14g	11	20
52	SbF ₅ /HF/H ₂	1150	14g	< 1	< 1
54	MoCl ₅	1300	-	8	16
55	WCl ₆	1300	-	6	12
61	SbBr ₃ /HBr	850	59g	43	~100
62	Ni(AA) ₂ /HCl	800	500	ND ^e	38
70	MoCl ₅ /HCl	800	500	< 1	4

^aIn this series of experiments, 5 g of coal was treated at 210°C for 5 hr in a rocking Teflon-lined autoclave. ^b Moisture-ash-free basis. ^c Unbeneficiated coal was used.

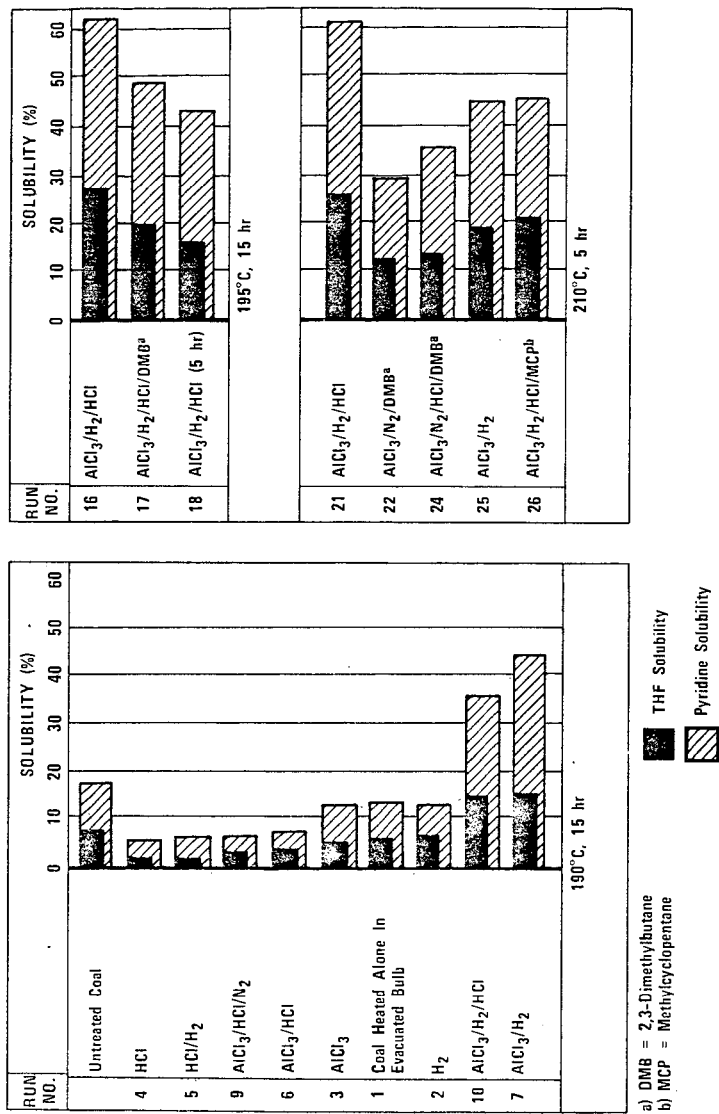
^d These experiments used 0.045 moles of catalyst per 4 g coal. A stirred Hastelloy C autoclave was used. ^e NO = Not determined.

ACKNOWLEDGEMENT

The financial support for this work from Energy Research and Development Administration under Contract No. E(49-18)-2202 is gratefully acknowledged.

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SA-4799-6

FIGURE 1 ACID-CATALYZED HYDROCRACKING OF BENEFICIATED ILLINOIS NO. 9 COAL

Particle Size Analysis in the SRC Process by Coulter Counter

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Introduction

This work was undertaken to develop an effective rapid technique for determining particle size of undissolved solids in the Solvent Refined Coal (SRC) Process. Particle size distributions for SRC filter feed from the Wilsonville SRC Pilot Plant and autoclave reaction mixtures from the Auburn Coal Conversion Laboratory were measured using a Coulter Counter Model TA.

The Coulter principle was originally applied to blood cell counting¹ and is now widely used in the biomedical area for cell counting and size distribution.² Industrial use of the Coulter technique is now widespread.³ The Coulter technique has been applied in coal research in the size analysis of pulverized coal, coal dust, and fly-ash.⁴ Presently, the Coulter technique is being applied to the study of particle size distributions in the SRC process. Interest in the effect of the mean particle size in the effluent from the SRC dissolver on filtration along with the problem of dissolver solids accumulation⁵ has shown the need for a reproducible method of determining particle size in SRC process streams.

Experimental

Equipment

Particle size determinations were performed on a Coulter Counter Model TA (Coulter Electronics, Hialeah, Florida) equipped with a Model TA External Size Calibrator II and an adjacent sample stand. The orifices normally used for the analyses were 100, 140, 200 and 280 μm .

Electron microscopy was performed using an AMR Model 1000 scanning Electron Microscope operating at 20KV with a tungsten source and an aluminum coated detector. The samples were coated with 60:40 gold-palladium using a Denton DV 502 vacuum evaporator. Optical microscopy was performed using a Wild Model M21 microscope equipped with a Polaroid MP-3 Land Camera.

Chemicals

Reagent grade ammonium thiocyanate (NH_4SCN) and dimethylformamide (DMF) obtained from Mallinckrodt prepared in a 5% solution was the electrolyte used for Coulter analysis. Metrical alpha -8 filters with 0.20 μm pore size were used for filtering the electrolyte solution. Carbowax 400 obtained from Union Carbide was the dispersant used for optical microscopy.

Procedure

Calibration of each orifice was performed using polystyrene calibration standards of known diameter (supplied by Coulter Electronics) dispersed in isoton.

Autoclave reaction samples and Wilsonville filter feed were sonicated using a low energy ultrasonic bath, dispersed in the 5% NH_4SCN - DMF electrolyte and again sonicated. The samples were diluted with electrolyte and immediately analyzed. For each sample 100,000 particles were counted and the particle size distribution was obtained. Extensive filtering with 0.2 μm filters was necessary to maintain the necessary background of the electrolyte.

For scanning electron microscopy samples were prepared by sonicating and further diluting the Coulter samples. The particles were filtered on a 0.2 μm filter and air dried. For optical microscopy, autoclave reaction mixtures were first sonicated and then dispersed in Carbowax 400. Hanging drop as well as slide preparations were used.

Verification

Verification of the Coulter technique by optical microscopy can be seen in Figure 1. Rigid polystyrene calibration spheres (9.99 μ m in diameter supplied by Coulter Electronics) were measured by optical microscopy under 500x magnification to have a diameter of 10.0 μ m. Subsequent analysis of the polystyrene's particle size by Coulter Counter agreed fully with the microscopy.

Results and Discussion

The Coulter technique measures the particle volume size distribution. The smallest particles measured had a diameter of 1.59 μ m with an overall diameter range of 1.59 to 128 μ m. All measurements were taken within the optimum range of the orifice. Particle size distributions were obtained for autoclave reaction mixtures and Wilsonville filter feed of Amax, Western Kentucky, Pittsburgh Seam, and Monterey coals. The particle size distribution measurements for each coal sample can be accurately reproduced within $\pm 10\%$. A mean particle size is obtained graphically by plotting the normalized cumulative particle volume percent versus particle diameter and then obtaining the mean particle size at the 50% volume level.

The initial mean particle size for unreacted coal was between 28.8 - 40.0 μ m. Table I shows the mean particle size in terms of particle diameter for four autoclaved coals reacted at 410°C for three different time intervals. Under autoclave conditions, the mean particle size varies significantly among the different coals. Within the time range studied the mean particle size for Monterey and Pittsburgh Seam coals remained essentially constant; however, the mean particle size of Western Kentucky coal increased with time while that of Amax coal decreased. The mean of Amax coal leveled off at 9.6 μ m after 4 hours. The temporal behavior of the particle size of each coal can be directly correlated to its dissolution rate and behavior. Both Monterey and Pittsburgh Seam coals dissolve very rapidly, leaving essentially only mineral matter after 15 minutes of reaction. Amax coal, however, is a slow dissolver which accounts for the decrease in particle size over the time period studied. Western Kentucky coal dissolves very rapidly but is sticky and adhesive; increasing reaction time allows the particles time to adhere to one another forming larger particles.⁶

The Wilsonville filter feed particle size distributions for each coal closely resembled the autoclave reaction distribution (an example is shown in Table II) except for Western Kentucky coal which showed a significant shift to smaller particles. Generally, the Wilsonville filter feed distributions showed greater variation within each sample than did the autoclave reactions resulting in a larger standard deviation for each volume range. A comparison of the mean particle size of Wilsonville filter feed to Auburn autoclave reaction mixtures is shown in Figure III. For each coal the mean particle sizes compare very closely with the exception of Western Kentucky coal. This difference can again be attributed to the adhesive nature of the Western Kentucky particles. In the filter feed the particles will tend to adhere to one another forming larger particles which stay in the dissolver while the smaller particles are elutriated out of the dissolver.

Optical and electron microscopy verified the presence, size, and character of the particles being counted by the Coulter Counter. Optical microscopy allowed observation of the particles in a solution matrix. Scanning electron microscopy permitted isolation of the particles from the oil matrix and allowed the particles to be individually observed. The unregular nature and individual character of the particles are shown in the micrographs in Figure 2-7.

Process Applications

Filterability of a solid/liquid slurry depends on the size distribution of the particulates entrained in the slurry as well as other factors such as viscosity, adhesive forces among the particles (i.e., whether the particles are sticky or discrete and unattractive) etc. A major objective of this work is to

determine whether mean particle size determined by Coulter Counter analysis can be correlated to filterability or, more specifically, cake resistivity. To this end: the mean particle size of particulates in the SRC dissolver effluent for the coals studied are compared with their associated cake resistivities.

Filtration rates for Amax, Western Kentucky and Monterey coal/oil slurries have been extensively studied under test conditions and without the incorporation of bodyfeed at the Wilsonville SRC Pilot Plant. Pittsburgh Seam coal/oil slurries have only been tested with bodyfeed. Table IV shows the cake resistivities calculated for the slurries run without bodyfeed. Indeed, correlations are evident between the ease of filtration (i.e., cake resistivity) and mean particle size. Amax coal/oil slurries which have the lowest cake resistivity and are, therefore, the most easily filtered of the three types of slurries considered have the largest mean particle size. Monterey coal/oil slurries have the highest cake resistivity, are the most difficult to filter, and have the smallest mean particle size. When screen blinding is taken into account, Western Kentucky ranks second in filterability as well as mean particle size. Cake resistivity is a function of the porosity of the cake which is directly related to particle volume. Particle volume is measured directly by the Coulter technique. In conclusion, the Coulter Counter can give a good indication of the filterability of a particular SRC process stream and, thus, should prove to be a useful tool in optimizing operational conditions for solids separation.

The present Coulter technique has two main limitations. First, since particles less than $1.6\mu\text{m}$ are difficult to detect, the total particle size range of the SRC effluents cannot be studied. The effect of the very small particles on filterability is not precisely known; however, it is very likely that particles below $2\mu\text{m}$ play a significant role in screen blinding. The second limitation is that carbonaceous agglomeration of SRC itself is difficult to detect because approximately 96% of SRC dissolves in the electrolyte. Detection of the formation of solid agglomerates would be highly desirable; for the accumulation of solids in the SRC dissolver has presented significant problems in processing certain types of coals, particularly those containing high concentrations of calcium. One reason for this accumulation, however, is commonly thought to be the formation and growth of calcium carbonate (CaCO_3) crystals. Inorganic agglomeration due to CaCO_3 crystal formation should be easily detectable by the Coulter technique presented herein since CaCO_3 is essentially insoluble in DMF.

On-line Coulter analysis of the SRC process stream would allow immediate detection of changes in the size distribution of the solvent stream particles. Through on-line analysis more precise correlations between mean particle size and filterability would be possible. Also, by monitoring the size distribution of particulates in the upstream and downstream to the filter, a direct reading on filtering efficiency could be obtained. Coulter analysis is also an effective method for determining the efficiency of other solid-liquid separation techniques, such as centrifuging and hydrocloning, currently being tested in the SRC process.

Acknowledgements

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TABLE I
Mean Particle Size of Autoclave Reacted Coals
at 15, 30 and 60 Minutes

Autoclave Conditions				
Temperature: 410°C				
Pressure: Hydrogen 2000 psi				
Solvent/Coal: 3/1				
Stirrer: 1000 rpm				
Time (min)	Mean Particle Size (μm)*			
	Amox	Western Kentucky	Monterey	Pittsburgh Seam
15	14.0	7.0	5.2	6.0
30	9.1	8.2	5.5	5.5
60	8.0	10.6*	4.8	6.0

*Through subsequent calculations, the population mean can be calculated. For example, Western Kentucky coal, reacted for 60 minutes, has a population of 2.0μm.

TABLE II
Particle Size Distributions of Amax Coal Autoclave
Reaction Mixture and Wilsonville Filter Feed

Particle Diameter (μm)	% Volume Distributions	
	Amax Autoclave 60 minute	Amax Wilsonville filter feed
1.59	10.9 \pm 0.6	10.4 \pm 1.8
2.00	8.7 \pm 1.2	6.3 \pm 1.4
2.52	6.6 \pm 0.64	5.7 \pm 0.6
3.17	5.5 \pm 0.35	6.7 \pm 0.7
4.00	5.6 \pm 0.36	7.6 \pm 0.8
5.04	6.4 \pm 0.42	9.3 \pm 0.7
6.35	6.9 \pm 0.49	8.6 \pm 1.0
8.00	8.2 \pm 0.57	8.8 \pm 1.1
10.08	9.0 \pm 0.68	9.2 \pm 1.3
12.7	9.7 \pm 1.6	9.2 \pm 1.7
16.0	9.2 \pm 1.5	5.7 \pm 0.8
20.2	7.0 \pm 1.8	4.6 \pm 2.0
25.4	4.6 \pm 2.6	4.6 \pm 2.8
32.0	1.3 \pm 1.0	2.3 \pm 2.7
40.3	0.6 \pm 0.05	0.6 \pm 0.1

TABLE III
Comparison of the Mean Particle Size
of Wilsonville Filter Feed and
Auburn Autoclave Reaction Mixtures

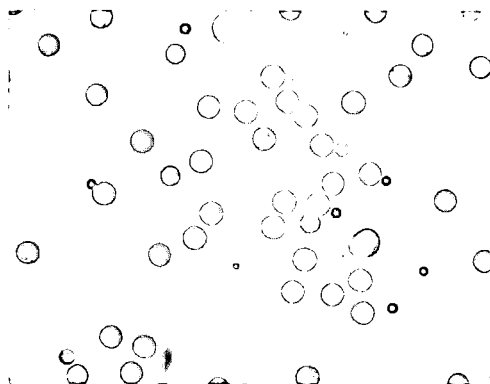
Coal Type	Date	Wilsonville Filter Feed Mean Particle Size	Auburn Autoclave Mean Particle Size
		μm	μm
Monterey	10-20-76	4.5	
Monterey	11-15-76	3.7	
Monterey	11-10-76	3.8	
Monterey	Average	4.0	4.8
Amax	- - - -	7.2	
Amax	12-19-76	6.4	
Amax	1-28-77	7.5	
Amax	Average	7.0	8.0
Western Kentucky	4-17-76	6.8	
Western Kentucky	5-29-76	4.6	
Western Kentucky	Average	5.7	10.6
Pittsburgh Seam	7-22-75	6.2	6.0

TABLE IV
Correlation between Cake Resistivity and Mean
Particle Size of Wilsonville Filter Feed

Coal	Cake Resistivity ft/lbm	ΔP (psi)	Mean Particle Size (μm)	
Amax	0.8×10^{12}	45	7.0	(Ref 7)
Western Kentucky	1.13×10^{12}	60	5.7	(Ref 8)
Monterey	1.22×10^{12}	60	4.0	(Ref 8)

Figure 1

Verification of
polystyrene particle
size



1 cm = 20 μm

Figure 2

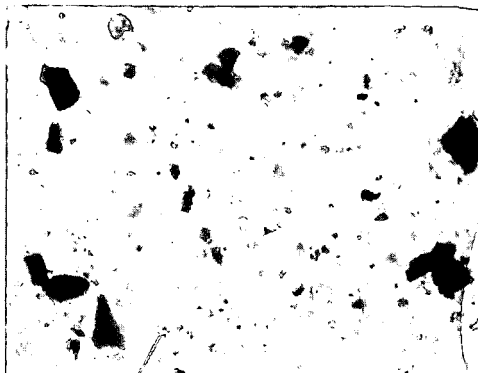
Photomicrograph of
Amax coal particles
(suspended in Carbowax)
after 60 minute autoclave
reaction (500x)



1 cm = 20 μm

Figure 3

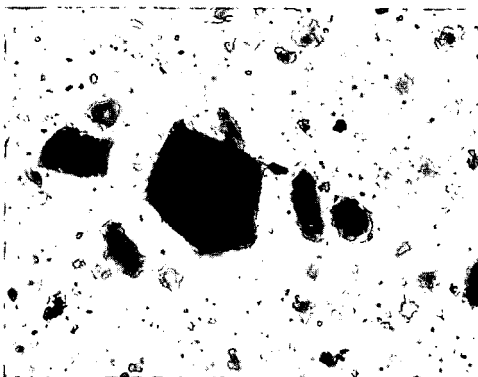
Photomicrograph of
Pittsburgh Seam coal particles
(suspended in carbowax) after
60 minute autoclave reaction
(500x)



1 cm = 20 μ m

Figure 4

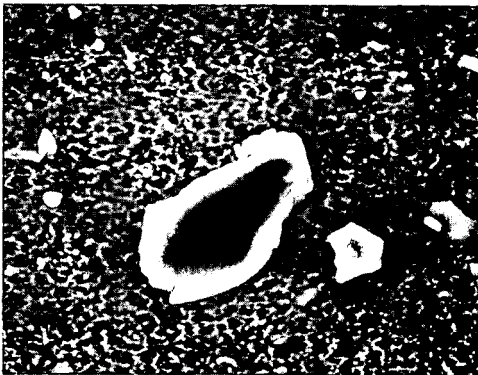
Photomicrograph of
Western Kentucky coal particles
(suspended in carbowax)
after 60 minute autoclave
reaction (500x)



1 cm = 20 μ m

Figure 5

Electronicrograph of
Western Kentucky coal particles
(on a Metrice1 filter)
after 60 minute autoclave
reaction (2000x)



1 cm = 5 μ m

Figure 6

Electronmicrograph of
Monterey coal particles
(on a Metrice1 filter)
after 60 minute autoclave
reaction (2000x)



1 cm = 5 μ m

Figure 7

Electronmicrograph of
Monterey coal particle
(on a Metrice1 filter)
after 60 minute autoclave
reaction (10,000x)



1 cm = 1 μ m

ENGINEERING DEVELOPMENT OF THE CITIES SERVICE,
SHORT RESIDENCE TIME (CS-SRT) PROCESS

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History and Development of the CS-SRT Process

Cities Service Research and Development Company (CSRD), the research arm of the Cities Service Company, has been developing a process scheme named The CS-SRT Process, for the non-catalytic, vapor-phase, hydrogenation of carbonaceous feedstocks. The initial and primary emphasis in our Energy Research Laboratory was to apply this technology to convert coal into pipeline quality gas and attractive byproduct yields of light aromatic (BTX) liquids.

A review of the literature early in 1974 led to our conclusion that the most productive area of process development would be that of short residence time hydrogenation. A brief literature review has been presented in our previous paper at the 1976 ACS (San Francisco) meeting (1).

In the summer of 1974, we designed a 1-4 lb/hr bench-scale unit capable of operation at temperatures and pressures that are scalable within present-day, commercial technology. A cold-flow model to test coal-hydrogen mixing injectors and to study coal-hydrogen slip velocities was designed and constructed in Autumn, 1974. Construction of the bench-scale unit began in December, 1974 and was completed in June, 1975 with the shakedown operations occurring in the Summer of 1975. The first complete material balance run was made in August, 1975. Since that time, over 125 runs have been made with a variety of feedstocks including lignite, bituminous and subbituminous coals, oil shale, tar sands and coal tars.

In September, 1974 work was initiated to estimate the economics in a conceptualized, commercial application of the CS-SRT Process for producing 250 MM SCFD of pipeline gas (and the associated byproduct BTX-liquids) from a mine-mouth plant in the Montana/North Dakota region. The results of this work pointed out the dramatic effect of benzene byproduct yield on lowering the cost of services for producing pipeline gas. In September, 1976, CSRD retained the Foster Wheeler Energy Corporation to perform a preliminary engineering design and cost study of the CS-SRT Process to validate the results of the earlier economic study. The results of this study will be reported in a separate paper.

Further development of the CS-SRT Process is being undertaken in several programs supported jointly by Cities Service, Rocketdyne Division of Rockwell International, and ERDA. Experimental tests are continuing in the bench-scale unit to explore conditions for maximizing liquids yields and also for maximizing gas (methane, ethane) yields. Process flowsheet studies are also being made. The next step of development of the CS-SRT Process would require about a 6-inch diameter, pilot plant reactor capable of processing about 100 TPD coal. This pilot-plant would be one scaleup step away from a 12-inch diameter, single tube, commercial-type operation.

This paper summarizes the analysis of the bench-scale data obtained when processing a North Dakota lignite. Some conceptual commercial processing alternatives which appear quite attractive are also discussed.

Experimental Apparatus

The bench-scale unit, as described in our previous paper, utilized initially a dilute-phase, free-fall reactor with a movable quench probe. Coal was delivered to the hydrogen-coal mixing injectors under gravity flow from a star-wheel, volumetric feeder fed by a lock hopper. The feeder-hopper assembly sat directly on top of the reactor.

Since the initial testing, a coal transport system was developed to improve the running efficiency of the test program. This system also allowed for the remote location and safe access of the coal feeding equipment in an adjacent laboratory pressure cell. The transported coal was separated in a cyclone immediately upstream of the coal-hot hydrogen injectors and carried into the reactor. The "cold" hydrogen was recycled back to a diaphragm compressor. The compressor diaphragms were protected against entrained solids by use of a settling chamber and filters located on the suction-side of the compressor.

Several other reactor designs were also incorporated into the bench-scale unit since the initial testing. A description of these reactors is shown in Figure 1. In these "entrained-flow" reactors, a wider range of values of several important parameters is achieved over that of the free-fall reactor:

	<u>Free Fall</u>	<u>Entrained-Flow</u>
Coal Flux, lb/hr ft ²	100-300	1500-35,000
Gas Velocity, fps	0.1-0.5	2-50
Particle Velocity, fps	0.5-8	2-50
Gas Reynolds No.	100-500	1000-6000
Particle Residence Time, sec.	0.10-4	0.05-10
Vapor Residence Time, sec.	2-30	0.05-5

The vertical entrained-flow reactor is used generally for very short residence time studies (less than 200 milliseconds) whereas the helical entrained-flow reactors are used for longer residence times (c.a., 1-5 sec.). All of the reactors used in the bench-scale unit are fabricated from stainless steel 316 alloy. A "hot wall" pressure reactor was used as the basis of design to expedite the testing program. The life of the hot wall reactor, even at the small diametral ratios used, is limited because of operation at high stress levels. Therefore, careful watch is maintained on the instantaneous creep strength of each reactor and preheater vessel. Reactors are removed from service before the cumulative approach equals 25% of the rupture time. All reactors are operated in the confines of a high-pressure, explosion-proof, laboratory cell with lockout controls during testing.

Temperature and Residence Time Measurements

Temperature of the coal-hydrogen stream is an extremely important variable affecting the rates of hydrolysis under short residence time conditions. Most experimenters involved in continuous, two-phase, coal-gas reactions report reactant or reactor temperature as maximum reactor wall temperature. This latter temperature can vary quite markedly from the reactant temperature depending upon the size and mass of the reactor, coal throughput, exothermicity of reaction, heat losses, etc. Accordingly, we have developed several multi-dimensional, computerized, heat transfer models for estimating reactant temperatures from reactor wall thermocouple readings. We have also used equivalent isothermal temperature (EIT) calculations to characterize the non-isothermal reaction conditions. EIT has been found to be a good characterization factor in correlating trends of hydrolysis yields with temperature.

Particle residence time is another extremely important parameter affecting hydrolysis yields, particularly under short residence time conditions. In the case of the free-fall reactor, particles traverse the reactor under the influence of both gravity and entrainment by hydrogen. Char settling velocities were calculated using the Stokes equation for narrow-size ranges of particles. Corrections were applied for the wider-range size distributions used in the bench-scale operation by calculating a surface-volume average particle diameter. Based on studies by Wen and Huebler (2), corrections for gas entrainment, uneven particle distributions and particle cloud density were also made.

For the case of entrained-flow reactors, particle residence times are directly correlated with the superficial hydrogen velocities. For both cases, a comprehensive experimental (cold-flow) program is underway in order to measure accurately particle residence times in both free-fall and entrained-flow reactors.

Coal Preparation

Wet North Dakota lignite was received in drums from the Grand Forks Energy Research Center. Prior to drying, the lignite was reduced to 1/2-inch x 0 particle size using a rotary jaw mill blanketed with nitrogen. Drying was done either in a laboratory, fixed-bed drier at 15" Hg vacuum or in an industrial, fluid-bed dryer, both under nitrogen blanketing. In both cases, the maximum lignite temperature was limited to 230-250°F. Moisture was reduced from 35% to less than 5%. The lignite was then pulverized using either a Sweco ball mill or a Mikropul hammer mill. In both cases, a nitrogen atmosphere was maintained. An 18-inch, continuous Sweco sieve, fed by a Syntrol vibrating feeder, was used to sieve the dried, pulverized lignite to specification.

Immediately prior to a run, the lignite charge to the unit was dried again, under vacuum, in the laboratory tray drier. An aliquot sample from a riffler was taken for every batch of coal fed to the bench-scale unit. The analysis of this sample was used as the basis for the material balance calculations for each run. A typical analysis was shown in our previous paper (1).

Material Balance Calculations

As a result of using hydrogen as both the preheating gas and the quenching gas, the coal-derived, reaction products are very dilute in hydrogen. Liquor and aromatic oils (boiling above BTX) are condensed using conventional indirect heat exchange. The lighter products, methane through BTX, are measured using gas chromatography combined with calibrated flow meters. Rotameters, orifice meters and turbine meters are used to measure gas flow. Redundancy in flow metering was incorporated into the design of the bench-scale unit in order to minimize uncertainty in calculation of the gaseous product yields.

All solid and liquid products are weighed after every run. The reactors were examined after each run and found to be free of deposits. The recovery system is purged with high pressure steam after every run in order to remove any hydrocarbons or char that does not readily disengage from the tubing surfaces, valves, receivers, etc. These hydrocarbons and char are recovered from the steam condensate by extraction with ether and are included in the material balance.

A packed cryogenic condenser was developed to condense the residual BTX material from the ambient (70°F) hydrogen stream after G. C. analysis. The weighed amount of BTX liquids recovered from this condenser checked

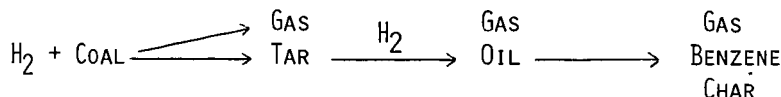
with the chromatographically-determined, BTX content of the gas stream entering the cryogenic condenser. Carbon balances of 90-105% are obtainable. Hydrogen consumption is calculated both 1) by difference of measured feed and product streams and 2) by elemental hydrogen balance between feed and product streams. Ash balances are 90-100%. The calculated oxygen balances are 100 \pm 10%. Nitrogen and sulfur balances are calculated by difference because of the very low quantities of these elements in lignite and lignite-derived, hydropyrolysis products. Gas yields are calculated based on coal fed to the reactor and corrected to 100% carbon balance.

CS-SRT Process Technology

Mechanism

The mechanisms involved in short residence time hydropyrolysis of coal are exceedingly complex. Coal consists of many types of structures each with different bond strengths. The initial coal conversion reactions are controlled by a thermal mechanism. Bond breaking will closely follow the rapid heating profile imposed on the coal. Weak bonds will rupture at the lower temperatures and decomposition products that are volatile will escape the particle under the driving force of a concentration or partial pressure gradient. As temperature is increased, stronger bonds will break and the volatiles will follow the same escape mechanism. These reactions are extremely rapid, of the order of milliseconds. Many of these devolatilized species are highly reactive and will undergo secondary decomposition reactions to form condensed and polymerized molecules generally classified as asphaltenes and char. However, these asphaltenes can be stabilized in the bulk phase and removed as single or double-ring aromatics by imposing the proper hydrogen partial pressure-temperature-residence time profile.

In terms of macro-reactions, the following simplified mechanism describes the vapor-phase, short residence time, hydrogenation process:



Although benzene is very stable, it too will decompose at elevated temperatures as shown by R. Graff and coworkers at CUNY (3). Extended residence times will also result in benzene decomposition as reported by Virk, et. al. (4). Normally, benzene decomposition in a hydrogen atmosphere would result in methane as the main decomposition product. However, it appears that in the case of benzene formation via short residence time coal hydropyrolysis, char particles catalyze the benzene-to-coke route of decomposition. Therefore, rapid quenching of the product vapors is necessary for the stabilization and recovery of aromatic liquids. The quantitative sequence of the in situ hydrogenation of tars to heavy oil to light aromatics is shown in Figure 2.

Coal Oxygen Reactions

Processing of lignite, because of its high oxygen content, provides some interesting observations about the mechanism of short residence time hydropyrolysis. The gaseous products obtained at very short residence time were rich in carbon dioxide while those obtained at longer residence time were depleted of essentially all carbon dioxide. This led to the conclusion that one of the initial reactions of short residence time

hydrogenation of lignite is the pyrolysis of carboxylic oxygen structures (decarboxylation). This agrees with the work reported by James Johnson at IGT (5). Once into the vapor phase, carbon dioxide hydrogenates to form carbon monoxide and water by the reverse water-gas shift reaction. Carbon monoxide will react further with hydrogen to form methane and additional water by the methanation reaction. These relationships are shown in Figures 3 and 4 which show the yields of water and methane respectively as a function of CO_2/CO ratio. The fact that these relationships were found in the 1/4-inch entrained-flow reactor and in the 1.1-inch, free-fall reactor, where the surface/volume ratio varied from about 50 to 500 in m^{-1} , tends to indicate that these vapor-phase reactions were not catalyzed by the SS 316 reactor wall. Equilibrium calculations of the reactor effluent also show that a) methane is approached from the carbon monoxide side of the steam-reforming reaction and b) carbon monoxide is approached from the carbon dioxide side of the water-gas shift reaction.

Coal Hydrogen Reactions

Another feature of the CS-SRT Process (as well as many other direct coal hydrogenation processes) is the utilization of coal hydrogen. Coal dehydrogenation increases continuously as hydrogenation severity and coal conversion are increased. During the initial pyrolysis stage of short residence time hydrogenation, the rate of coal dehydrogenation is increasing faster than hydrogen is being consumed. The rate of coal dehydrogenation appears to reach a maximum at about 30% carbon conversion as shown in Figure 5. At this point, approximately 50% of the hydrogen consumption is coming directly from the coal. This point also corresponds to the end of the pyrolysis mechanism and the initiation of the char hydrogenation stage. This is not surprising since 30% carbon conversion corresponds to 43% coal (MF basis) conversion which is identical to the ASTM volatile matter for lignite.

Furthermore, at carbon conversions greater than about 30%, hydrogen partial pressure has a pronounced effect on carbon conversion. The flux of volatiles escaping the coal particles decreases greatly above the 30% carbon conversion level. This results in increased hydrogen counterdiffusion into the char structure allowing more reaction between hydrogen and carbon sites. Higher hydrogen pressures greatly influence the diffusion of hydrogen into the particle. This is shown in Figure 6 and agrees with the work of James Gray and coworkers at PERC (6).

Rapid-Rate Carbon

One of the principal correlation tools of short residence time hydrolysis is the rate of conversion of rapid-rate carbon (7). The latter is a measure of the total theoretical amount of coal carbon that can be converted under "rapid" hydrogenation conditions. The rate itself is proportional to hydrogen partial pressure and the amount of rapid-rate carbon material remaining. Rapid-rate carbon is a function of coal type, particle size, temperature and pressure and is a difficult parameter to measure. Although this kinetic tool cannot be used as a predictive technique unless all of these functionalities are known, it can be used to demonstrate the relative effects of different hydrolysis data acquisition methods.

When processing a lignite at about 850°C , researchers (7) utilizing a captive sample technique for data acquisition reported a pseudo-rate constant of $50 \text{ atm}^{-1} \text{ hr}^{-1}$. Calculation of the pseudo-rate constant from free-fall reactor test data reported in the literature (8) results in a value of about $8 \text{ atm}^{-1} \text{ hr}^{-1}$ for lignite. Both sets of data were based on the assumption that the rapid-rate lignite carbon available for rapid hydrogenation is 100%. If the actual rapid-rate carbon for lignite is less

than 100%, then the respective pseudo-rate constants would both show corresponding increases.

The pseudo-rate constant for lignite at 850°C for the CS-SRT Process is 230 atm⁻¹ hr⁻¹, 5 to 30 times greater than that of the literature data, respectively. This CS-SRT pseudo-rate constant was based on data obtained with the turbulent, entrained-flow reactor equipped with a highly efficient, coaxial, coal-hydrogen mixing injector. Thus, it can be seen that in order to maximize carbon and thermal efficiencies in the conceptual CS-SRT reactor, it is imperative to utilize a reactor design based on data acquired from a bench-scale unit that has been operated under conditions closely scalable to the commercial reactor concept.

CS-SRT Conceptual Process

A conceptual plant design for producing 250 MM SCFD of pipeline gas and 6300 BPD of aromatic liquids has been developed. The design was based on data obtained when processing a North Dakota lignite in the bench-scale unit. Several alternative processing sequences have been examined but an optimization has not been undertaken. When more definitive test data become available, as would be generated in a pilot plant, a conceptual process optimization will be performed. The balance of this paper deals with the processing requirements about the reactor system including coal drying, coal feeding, SRT reactor designs and quench. Details of the downstream processing, hydrogen production and offsites are presented in another paper at this meeting.

Design Basis

After careful analysis of the CS-SRT Process data and patents, the following reactor design basis was established for the conceptual plant:

1. "Slow" heating of coal to the incipient devolatilization temperature in order to increase thermal efficiency;
2. "Rapid" heating of coal from the incipient devolatilization temperature to hydrogenation temperature in order to maximize rate of conversion;
3. Use of the reactant, hydrogen, as the heat carrier in order to minimize the number of streams to be handled;
4. Total residence time less than two seconds;
5. Rapid quenching of product vapors to prevent secondary decomposition reactions;
6. Recovery of high temperature heat from the reactor effluent.

Coal Drying

Lignite drying on the commercial-scale typical of an SNG plant has an energy requirement of about 16 billion BTU/day which equates to about 5.5% of the heating value (HHV) of the lignite. In conventional drying methods, this heat is supplied from hot combusted fuel gas. Efficient lignite drying is a relatively new technology and conventional processes have been applied to reducing the moisture from 35% to only about 10-15%. In the case of the CS-SRT Process, any moisture entering the reactor will be evaporated at the relatively high SRT reaction temperatures. This heat duty will of course come from the hot recycle hydrogen stream. Therefore, a design specification of 3% lignite moisture was set in order to improve the reactor heat balance. Reduction to 3% using conventional drying technology may prove difficult due to the long residence times required in gas conveyor-type dryers.

To circumvent these problems, coal drying in the CS-SRT Process will make use of the large quantity of low level heat available in the form of 60 psi steam. This steam is associated with the inefficiencies in the

many processing steps in all coal conversion plants. In the CS-SRT Process, it is believed that 60 psi steam will account for about 5% of the heating value of the coal fed to the plant.

Furthermore, advantage is taken of the boiling point depression of water as a result of the azeotrope formed between water and benzene (156°F, 1 atm, 30 mol% water, 70 mol% benzene). Benzene is chosen since it is a byproduct of the CS-SRT Process thereby minimizing the handling of additional chemicals. Accordingly, wet lignite will be pulverized and slurried with benzene as shown in Figure 7. The slurry will then be fed to an ebullated-bed contactor where it is heated by an inert recycle gas stream. The gas stream will obtain its heat by indirect heat exchange with the 60 psi steam source. Proper design of the ebullated-bed, which falls within Cities Service's LC-Fining technology, will result in the vaporization of the benzene-water azeotrope. Condensation of the azeotropic vapors results in the recovery of a relatively pure liquid benzene stream and a liquid water stream. The benzene is recycled and this water, generated internally within the process, will be available for plant use in the gasifiers or shift reactors. This water can account for approximately 40% of the total process water needed in the CS-SRT complex and can result in water savings of about 2000 acre-ft/yr.

The "dried" coal-benzene slurry will be drawn from the ebullated-bed with less than 3% water content. The slurry will now readily be available for downstream processing in the coal feed section.

Coal Feeding

Since the CS-SRT Process utilizes a pressurized gasifier, it has the same problems regarding the feeding of coal into a pressure vessel as do other pressurized gasification processes, such as BI-GAS, HYGAS, and SYNTHANE. One major difference and advantage is that the CS-SRT Process produces benzene, a solvent that can be used to maintain a pressure seal. Therefore, the low pressure, lignite-benzene slurry from the coal drying section will be pumped to system pressure with a positive displacement injection pump. The benzene will be subsequently flashed away from the lignite in a drier near its critical point. Benzene content of the dried coal should be extremely low as a result of the purging effect of the benzene-free, fluidizing gas.

Lignite with less than 3% water and at system pressure will then be delivered to a dense-phase transport system (see Figure 8) similar to that described by Rocketdyne Division of Rockwell International (9). Laboratory tests have shown lignite dried from a benzene slurry to be free-flowing. It is believed that the small quantity of benzene remaining in the coal pores will enter the reactor and be carried through along with the product gases without undergoing decomposition.

Reactor Design

Rapid heating of coal may be achieved by mixing hot recycle hydrogen with the dense-phase, transported coal in an injector assembly at the inlet of the reactor. With properly designed injectors, mixing is rapid on the order of a few milliseconds. Once mixed the coal and hydrogen will traverse the reactor upwards under conditions of fast fluidization to allow intimate contact between hydrogen and coal particles. The temperature and flowrates of the hot recycle gas and coal respectively will be set to allow the CS-SRT reactions to proceed adiabatically and exothermically. The recycle hydrogen/coal ratio is a critical parameter affecting not only the reactor heat balance and reactor kinetics but also the cost of downstream processing equipment.

As a result of the rapid heatup and short residence time features of the CS-SRT Process, extremely high coal throughputs are possible, of the order of 2000 lb/hr ft³ of reactor volume. For the case of a 250 MM SCFD

plant (and associated BTX production), only three reactors will be required, each capable of processing roughly 200 TPH coal through a 3 1/2 ft inside diameter.

Multi-Tube Reactor Concept

The combination of operating at a minimum hydrogen/coal recycle ratio under exothermic conditions can result in excessive temperature rises. This could result in loss of valuable benzene due to the adverse kinetics favoring benzene decomposition. Furthermore, since coal is being transported in dense-phase in a series of tubes to a multi-element injector assembly, a multi-tube reactor concept appears plausible.

Accordingly, a multi-tube, high pressure reactor with internal heat exchange is being developed. High pressure steam generation (1500 psi) can be used on the coolant side to maintain an isothermal tube wall. However, by using a coolant, such as a molten metal, heat can be absorbed non-isothermally while allowing control of the temperature profile within the reactor tube. This heat can also be used for high temperature heat exchange elsewhere in the process. Control of the reactor temperature profile will afford the plant operator the ability to vary product spectrum, conversion and turndown.

In one conceptual case, molten sodium is used to 1) control the reactor temperature profile and 2) limit tube wall temperature in contact with coal-hydrogen reactants to 1200°F. Other molten metal systems, such as molten lead or a 22% sodium/78% potassium eutectic, are also under consideration. The reactor design might consist of 12 alloy heat transfer tubes containing the reactants at system pressure. The tubes are immersed in the molten metal environment, also at system pressure, within a refractory-lined pressure vessel. The tubes will be about 12-inches in diameter and fit within the 3 1/2 ft. i.d. vessel. The major advantages of this reactor design are believed to be:

1. High coal throughput per volume of reactor;
2. Excellent turndown (8-100% full capacity);
3. Excellent reactor temperature control;
4. Overcomes heat transfer limitations of conventional pressure vessels;
5. Potential low risk to scaleup from pilot operations.

Molten Metal Heat Exchange

High thermal efficiency in the CS-SRT Process may be achieved by recovery of the high temperature heat of the reactor effluent. However, this has to be accomplished within the constraints of rapid quenching. This problem has been recognized and solved in the associated technology of ethylene production via steam cracking (10,11). In the latter reference, indications are that molten metal is used to rapidly quench steam cracker effluent while at the same time recovering high temperature heat. Quenching requirements for ethylene production are even more stringent than for the CS-SRT Process, of the order of 10-15 milliseconds compared to about 100 milliseconds.

A molten metal heat exchanger system has been conceptualized and applied to the CS-SRT Process. The bulk of the heat stored in the molten metal results from heat recovery in the reactor effluent quench exchanger. This heat can then be exchanged to provide the duties for recycle gas preheating, coal moisture removal and coal-benzene slurry drying. These total duties are equivalent to about 7.5 thermal efficiency points.

Our calculations have shown that this concept is feasible from both a process and a metallurgical standpoint. The concept utilizes molten metal technology already developed for the Clinch River breeder reactor.

Studies of the economics and optimization of this molten metal technology to the CS-SRT Process are continuing.

Conclusion

Bench-scale testing with a North Dakota lignite has shown that the CS-SRT Process scheme may be an attractive process for converting coal to pipeline quality gas, ethane and BTX liquids. Production of BTX liquids (and ethane feedstock for ethylene production) in the CS-SRT Process is a key factor in lowering the overall cost of services for producing SNG from coal. As a result of the rapid heatup, short residence time and rapid quench features of the process, a simple, high throughput reactor concept may be utilized without suffering loss in conversion and undesirable, secondary-decomposition reactions.

In order to maximize carbon and thermal efficiencies in the conceptual CS-SRT reactor, it is imperative to utilize a reactor design based on data acquired from a bench-scale unit that has been operated under conditions closely scalable to the commercial reactor concept.

Flowsheet studies of the CS-SRT Process have resulted in identifying several promising processing steps applicable to coal gasification:

1. Drying of coal using azeotropic benzene vaporization in an ebullated-bed contactor;
2. Multi-tube, high pressure, entrained-flow reactor concept with internal heat exchange and low scaleup ratio to commercial operation;
3. High temperature, heat recovery using molten metal heat exchange.

The next step of development of the CS-SRT Process would require about a 6-inch diameter, pilot-plant reactor capable of processing about 100 TPD coal. This pilot-plant would be one scaleup step away from a 12-inch diameter, single tube, commercial-type operation.

Acknowledgements

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Figure 1

COMPARISON OF REACTORS UTILIZED IN ENERGY RESEARCH LABORATORY

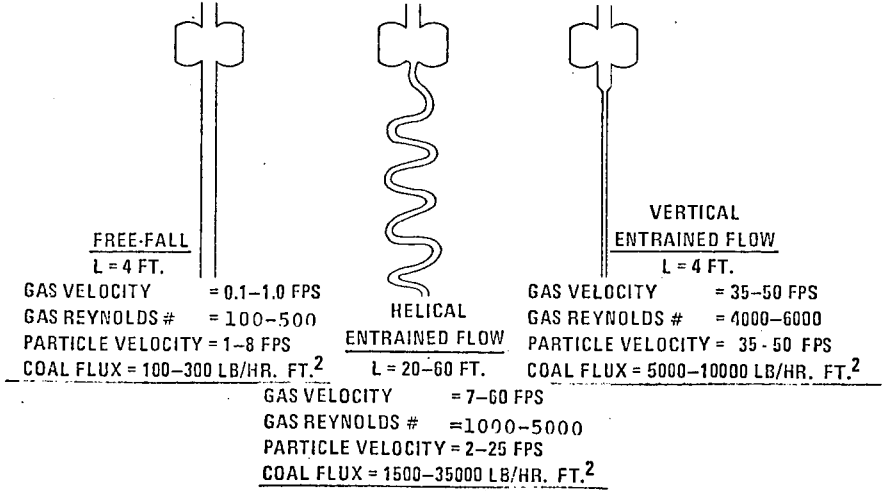


Figure 2

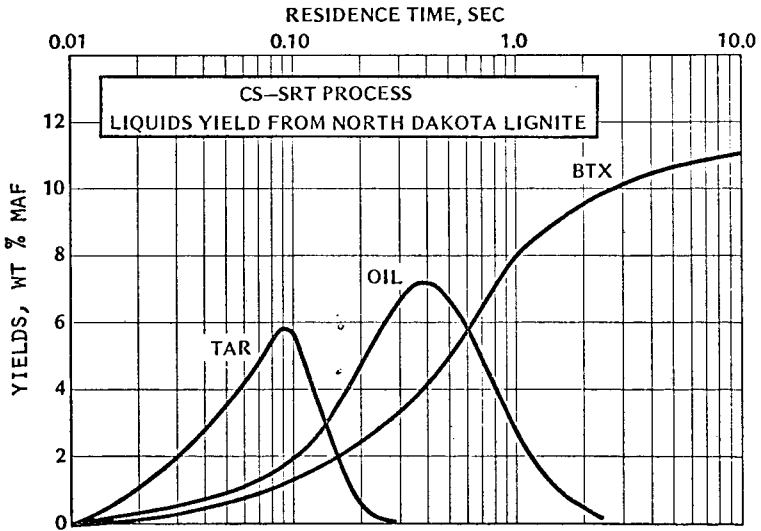


Figure 3

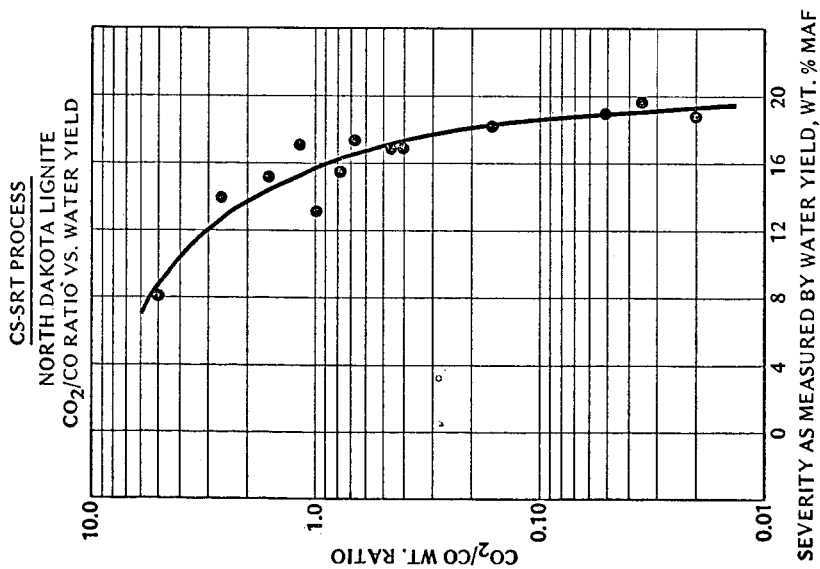


Figure 4

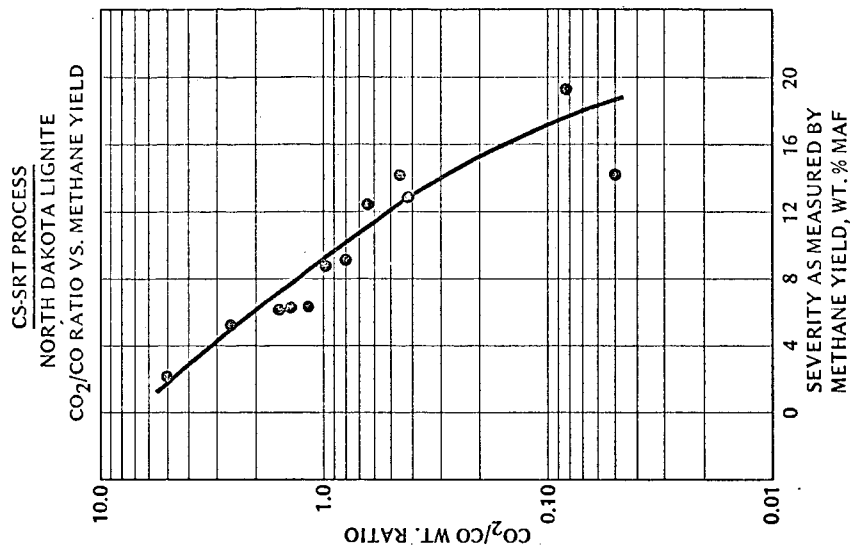


Figure 5

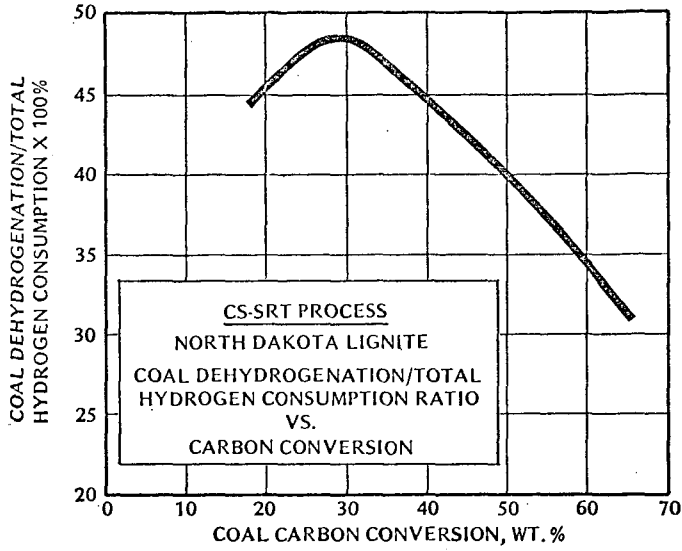


Figure 6

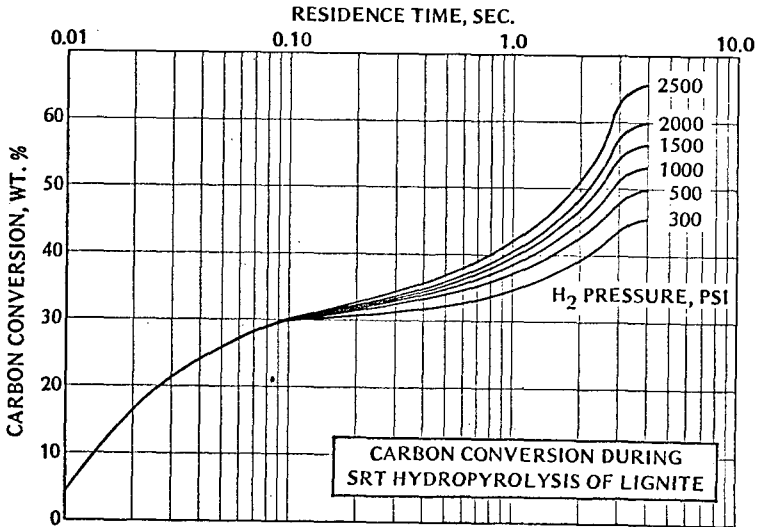


Figure 7
CS-SRT PROCESS
Coal Drying

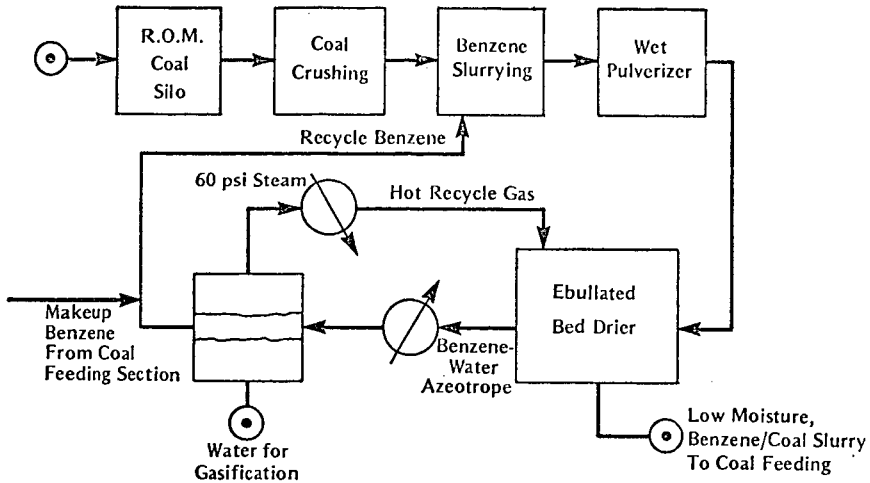
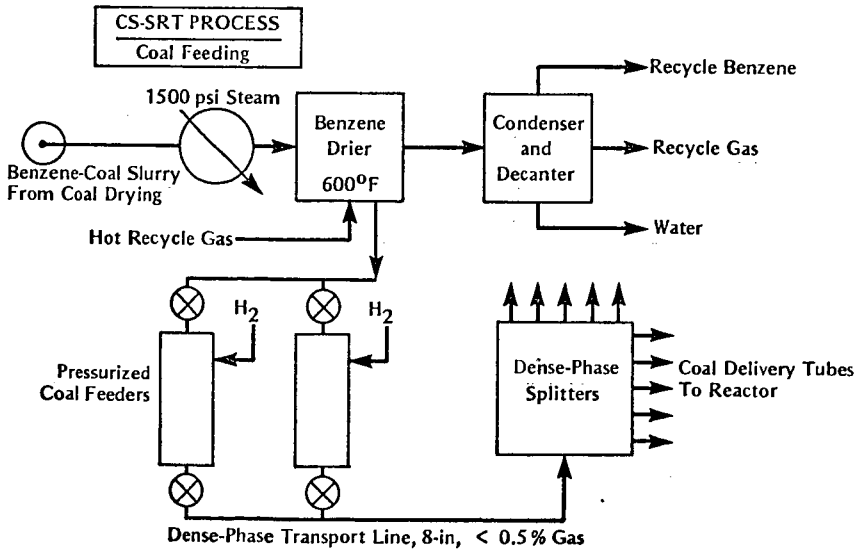


Figure 8



LIQUID FUELS FROM LOW Btu GAS: DILUTE PHASE FISCHER-TROPSCH SYNTHESIS

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Methods of producing liquid hydrocarbons from coal and other solid carbonaceous substrates may be roughly characterized as direct or indirect. Direct methods include various pyrolysis and catalytic hydrogenolysis techniques which are described in the literature (1,2). Indirect liquefaction methods first gasify the carbonaceous substrate to produce a synthesis gas which can then be converted into liquid hydrocarbons. The composition of the synthesis gas can be tailored to fit the needs of the subsequent hydrocarbon synthesis by proper choice of gasifying conditions, gasifying agents, CO-shift conversion and removal of undesirable constituents. Extensive investigations have been made on the use of synthesis gas composed of H_2 and CO for producing liquid hydrocarbons suitable as fuel and specialized chemicals. These reactions are categorically referred to as the Fischer-Tropsch synthesis although significant contributions have been made by a number of different investigators. The Fischer-Tropsch synthesis has been almost exclusively used with synthesis gas consisting of pure H_2 and CO of various stoichiometric ratios. In the following discussion a new application of this old technology for indirect coal liquefaction will be presented. This application consists of using synthesis gas diluted with inerts such as N_2 , CH_4 and CO_2 and is referred to as the Dilute Phase Fischer-Tropsch Synthesis.

CONVENTIONAL FISCHER-TROPSCH SYNTHESIS

The synthesis of hydrocarbons from H_2 and CO has been of considerable academic and practical interest since the discovery of methane synthesis by Sabatier in 1902. These simple reactants constitute the necessary building blocks for producing a large spectrum of essential organic chemicals and fuels. The synthesis has been reviewed several times over the past 50 years by Vannice, (3) Pichler, (4) Anderson, (5,6) Hofer, (7) and Storch et al. (8)

The diversity of the conventional Fischer-Tropsch synthesis is demonstrated in Figure 1. It is evident that a considerable spectrum of hydrocarbons can be obtained from pure H_2 and CO synthesis gas by proper choice of reaction conditions. The choice of catalyst is perhaps the most critical variable in the synthesis although pressure, temperature, H_2/CO ratio and space velocity or residence time are clearly important in determining product composition. Methane is the predominant product with nickel catalysts over a considerable pressure range at 200-300°C. Paraffins and olefins are produced over iron and cobalt catalysts in both the low (1 atm) and medium (5-20 atm) pressure synthesis at 185-300°C. At higher pressures (~ 100 atm) and temperatures ($\sim 400^\circ C$) the product over iron catalysts consists mostly of oxygenated hydrocarbons (Synthol). High molecular weight (100,000-200,000) paraffins are produced with ruthenium catalysts at 100-1000 atm pressure and 200-250°C. Methanol and higher alcohols are obtained from zinc oxide and alkali promoted zinc oxide catalysts, respectively, at high pressures (100-300 atm) and temperatures of 250-350°C. Using difficult to reduce metal oxide (ThO_2 , $Al_2O_3 + ZnO$) catalysts at high pressures and temperatures of 400-500°C aromatics, naphthenes and iso-paraffins are produced.

DULITE PHASE FISCHER-TROPSCH SYNTHESIS

In spite of the extensive work on the Fischer-Tropsch synthesis, little attention has been directed at employing diluted synthesis gas in the synthesis. Dilute synthesis gas is similar in composition to low Btu gas. It is obtained by gasifying carbonaceous material with air-steam or oxygen enriched air-steam mixtures. Contrary to gasification with O_2 -steam, the gas will contain moderate to high concentrations of nitrogen. The work that has been done with dilute synthesis gas, although sketchy, indicates that significant yields of liquid hydrocarbons can be obtained with conventional Fischer-Tropsch catalysts. Hall and Smith (9) examined the effect of nitrogen dilution on the F-T synthesis; the results are summarized in Table 1. As with non-diluted synthesis gas at constant temperature, the yield of product per volume of synthesis gas decreased with increasing space velocity. Furthermore, at constant space velocity replacement of synthesis gas with nitrogen results in an increase yield of liquids plus solids per cubic meter of $2H_2 + 1CO$. This is readily seen by comparing yields of the first with the second row at 1 atm and the fourth with the fifth row for the 10 atm synthesis. Gibson and Hall (10) studied the F-T synthesis with diluted synthesis gas over a Co-ThO₂-MgO-kieselguhr catalyst concluding that the dilution affected the rate of synthesis by reducing the partial pressure of reactants ($2H_2 + 1CO$). Dilution of the synthesis gas was also observed to increase the proportion of the low-boiling product. The observed variation in liquid product and CO conversion with dilution by these investigators is shown in Figure 2. Although the yield per unit volume of gas will be less in the dilute phase F-T synthesis, the product composition is likely to be similar to conventional F-T synthesis under similar operating conditions. A typical product composition over a cobalt catalyst in the conventional F-T synthesis is shown in Figure 3.

UTILITY OF DILUTE PHASE F-T SYNTHESIS

In the preceding section we have shown that dilute phase F-T synthesis can be used to obtain liquid hydrocarbons from synthesis gas ($H_2 + CO$) that is highly diluted with N_2 , CH_4 and CO_2 . With this capability, the dilute phase Fischer-Tropsch synthesis is viewed as an add-on facility where liquid hydrocarbons are obtained as a byproduct from low Btu gas. Although any low Btu gas could be used in the synthesis, in situ generated low Btu coal gas has been used to carry out preliminary engineering and economic feasibility studies. The conceptualized process is shown in Figure 4. Stepwise, coal is first gasified in situ with air. The in situ generated gas is then subjected to a gas clean-up where H_2S , H_2O , CO_2 and dust are removed. This is followed by dilute phase F-T synthesis and product fractionation to obtain the liquid hydrocarbon byproduct from the low Btu gas. Material balance calculations based on situ coal gasification data by Brandenburg et al. (13) and the dilute phase F-T synthesis data of Gibson and Hall (10) for a 50,000 bbl/da plant are shown in Table 2. Hence, 86×10^8 SCF/da of air is used for the in situ gasification of 2.16×10^5 ton/da of coal. The removal of impurities provides 147.7×10^8 SCF/da of dry, dilute, low Btu (152 Btu/SCF) synthesis gas. Dilute phase F-T synthesis yields 50,000 bbl/da of liquid byproduct with the primary product being 121.0×10^8 SCF/da of low Btu (148 Btu/SCF) fuel gas. The liquid yield amounts to 1/4 bbl/ton of in situ coal gasified. The liquid would be sulfur and nitrogen free and estimated to contain up to 25% olefins with 57% boiling below 150°C and 34% boiling between 150-270°C.

TABLE 1. Effect of Diluted Synthesis Gas on F-T Synthesis⁽⁹⁾
(Co-ThO₂-MgO-kieselguhr catalyst)

Temperature °C	Pressure atm	Feed Gas Composition					Space Velocity hr ⁻¹	Yield of Liquids and Solids	
		volume %						g/m ³	
		H ₂	CO	N ₂	CO ₂	CH ₄		Feed Gas	2H ₂ +1CO
193	1	68.7	30.0	1.0	--	0.3	184	109.2	110
193	1	58.2	24.2	16.3	--	1.3	91	106	127
193	1	44.4	26.7	28.8	--	0.1	133	87.8	123
192	10	62.0	31.5	4.0	2.5	--	131	106	113
193	10	41.8	20.0	35.1	3.1	--	138	112	120

TABLE 2. Process Stream Compositions

Process Stream #	Description	Composition, Vol. or Wt. %	Flow
1	Air	80 N ₂ , 20 O ₂	86 x 10 ⁸ SCF/da
2	Coal	6.3 H ₂ O, 18.4 ash, 0.5 S, 4.6 H, 55.3 C, 0.7 N, 14.2 O	2.16 x 10 ⁵ tn/da
3	Low Btu gas (102 Btu/SCF)	26.9 H ₂ O, 12.2 H ₂ , 6.1 CO, 0.6 O ₂ , 36.5 H ₂ , 3.3 CH ₄ , 0.4 C ₂ , 14.0 CO ₂ , 0.05 H ₂ S	253 x 10 ⁸ SCF/da
4	Scrubbed gas impurities	? dust, 0.12 H ₂ S, 64.8 H ₂ O, 35.0 CO ₂	105 x 10 ⁸ SCF/da
5	Dry dilute phase synthesis gas (152 Btu/SCF)	20.7 H ₂ , 10.3 CO, 1.0 O ₂ , 61.8 N ₂ , 5.6 CH ₄ , 0.7 C ₂	147.7 x 10 ⁸ SCF/da
6	Synthesis product and unconverted gas	0.35 C ₁ H _{2.4} (estm.), 8.1 H ₂ , 4.6 CO, 69.6 N ₂ , 6.5 CH ₄ , 1.7 C ₂ , 8.8 H ₂ O, 0.2 C ₃ , 0.2 C ₄	133.6 x 10 ⁸ SCF/da
7	Liquid hydrocarbon	C ₁ H _{2.4} (estm.), density = 0.85 g/cm ³ (estm.)	5 x 10 ⁴ bbl/da
8	Low Btu gas (148 Btu/SCF)	8.9 H ₂ , 5.1 CO, 76.5 N ₂ , 7.1 CH ₄ , 1.9 C ₂ , 0.2 C ₃ , 0.2 C ₄	121.0 x 10 ⁸ SCF/da
9	Water	100 H ₂ O	11.9 x 10 ⁸ SCF/da

PROCESS ECONOMICS

Preliminary economics have been calculated for the conceptualized dilute phase F-T synthesis coupled with in situ coal gasification. These calculations, based on the material balance shown in Table 2 and certain necessary assumptions, indicate that high quality sulfur-free liquid fuels can be produced for as little as \$13/bbl. This assumes use of an iron catalyst costing \$0.10/lb, low Btu gas from in-situ gasification at \$0.43/MM Btu as described by A. D. Little, (11) and a 10% return on capital investment.

The cost of the liquid fuel produced is highly dependent on capital investment and raw materials costs so any increase in space velocity or increase in yield would significantly reduce the cost of the liquid product. Likewise an increase in the cost of raw materials (low Btu gas, catalyst, etc.) would increase the liquid fuel cost. The influence of these variables on liquid fuel cost is shown in Table 3. These liquid fuel costs are based on a 10% return on investment and a six month catalyst life. Two different space velocities, 1000 hr⁻¹ and 2000 hr⁻¹ have been used in the calculations. The parenthesized cost figures are for the 2000 hr⁻¹ space velocity operations. The economic incentive for operating at higher space velocities or larger through-puts is clearly evident from the data in Table 3. It is also evident from the tabulated data that as the catalyst cost increases so does the benefit from operating at higher space velocities.

TABLE 3. Liquid Fuel Cost

	Product Cost \$/bbl		
	Cost of Low Btu Gas \$/MM Btu		
<u>Catalyst Cost</u>	<u>\$0.43</u>	<u>\$0.75</u>	<u>\$1.00</u>
\$0.10/lb	13 (12)	18 (16)	21 (20)
\$1.00/lb	23 (16)	28 (21)	32 (25)

Total capital investment for a dilute phase F-T facility producing 50,000 bbl/da of liquid fuels would be \$300-400 million in 1976 dollars. The major processing unit required is the synthesis reactor. Cost of the reactors is about one third of the total capital investment because of the large heat transfer area required to maintain proper control of reaction temperature. The heat of reaction will be recovered by generating steam to be used as process feed, in steam driven pumps and compressors, and for electrical power drives. Types of reactors that could be used range from a simple vertical boiler with catalyst packed in the tubes to a design where the catalyst is sprayed on the heat transfer surface. (12)

CONCLUSIONS

The dilute phase F-T synthesis is a new application of old technology. It provides a means of obtaining significant yields of liquid hydrocarbon byproduct from low Btu gas. Since the low Btu gas is obtained by gasifying with air in place of oxygen the need for separating O_2 and N_2 is eliminated. Engineering and economic evaluations were made of dilute phase F-T synthesis coupled with in situ coal gasification. The complex was scaled to produce 50,000 bbl/da of liquid byproduct and 121×10^8 SCF/da low Btu (148 Btu/SCF) fuel gas primary product. Considering such economic factors as return on capital investment, catalyst cost and life, space velocity and low Btu gas cost, the liquid product cost was estimated to be between \$13-35 bbl. The most significant contributions to the product cost were identified as return on investment, capital cost and catalyst cost. Technical indications are good that significant reductions can be made in the latter two areas which will improve the overall economics.

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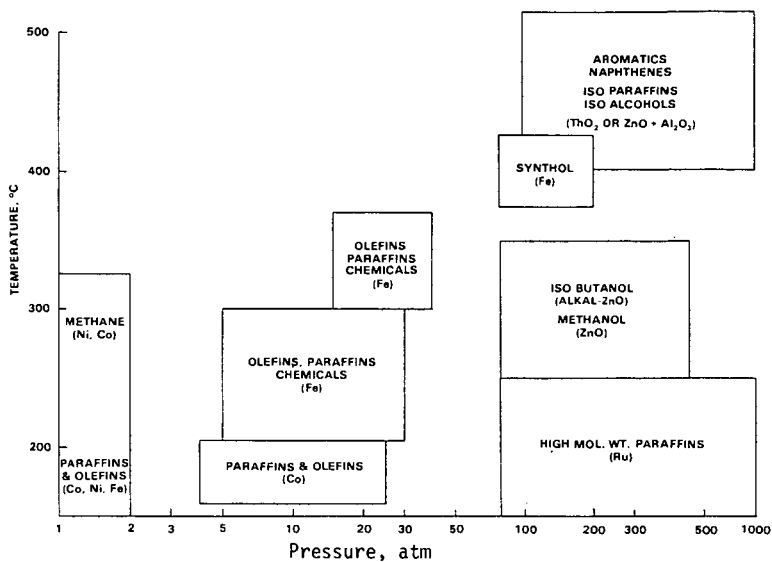


FIGURE 1. Pressure-Temperature Regions for Synthesis with CO and H₂

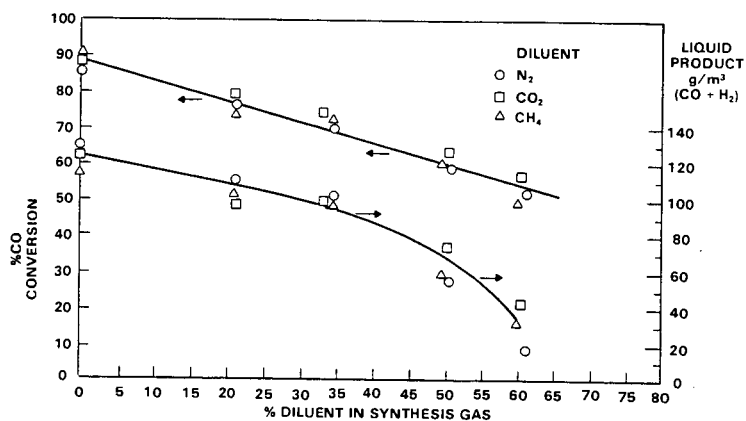


FIGURE 2. Dilute Phase Fischer-Tropsch Synthesis (Co-Catalyst, 1 atm, 185°C, 2H₂/lCO, 900 hr⁻¹ Space Velocity)

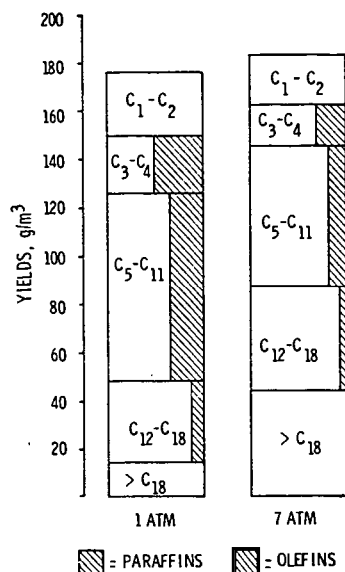


FIGURE 3. Typical yields with Co-ThO₂-MgO-kieselguhr catalyst at 1 atm. and 7 atm.

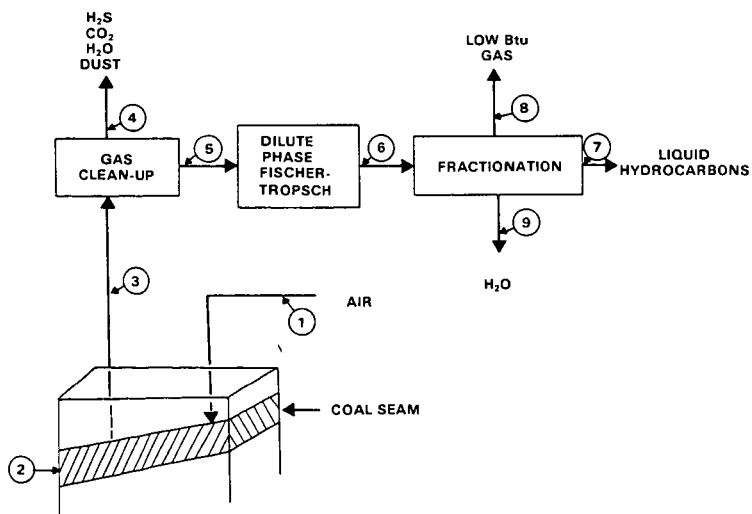


FIGURE 4. Dilute Phase Fischer-Tropsch Synthesis for In Situ Coal Gasification

ECONOMIC COMPARISON OF COAL FEEDING SYSTEMS IN COAL GASIFICATION--LOCK HOPPER VS SLURRY

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INTRODUCTION

Coal feeding to the various pressurized coal gasification processes presents certain technical problems that will have to be solved. Two feeding systems being considered are the lock hopper and coal slurry. The coal slurry system has the advantage of being simple to operate with a good reliability, but erosion problems in the circulating pumps and injection valves will have to be solved. The lock hopper system has the advantage of feeding a dry coal without solvent dilution, but will also have erosion problems in the valves and will require a complex cycle control system.

An economic comparison was made of the two feeding systems based on the Bituminous Coal Research's Bi-Gas process using a Western Kentucky No. 11 coal, assuming the two systems are technically feasible. The estimates are based on January 1976 cost indexes. Average selling prices of the gas were determined by using discounted cash flow rates of 12, 15, and 20 percent at various coal costs. No inflation factors are considered for the life of the plant. Pollution abatement considerations have been incorporated. Some of the economic and technical details of the Bi-Gas process are included.

Lock Hopper System

The Bi-Gas process is a two-stage coal gasification system to convert bituminous and subbituminous coal to a high-Btu pipeline gas. Figure 1 is a flowsheet of the process (1) and includes the following steps:

1. Coal preparation, which includes crushing, screening, sizing of the run-of-mine coal, and conveying the sized coal to the lock hopper feeding system (2) (not shown in figure 1).
2. In the upper section of the gasifier, coal contacts the hot synthesis gas produced in the lower section and is partially converted to methane and more synthesis gas. The entrained char in the raw product gas is separated and recycled to the lower section, where it is gasified to produce synthesis gas and heat required in the upper section.
3. Shift conversion of the synthesis gas to $H_2:CO$ ratio of 3.1:1.
4. The hot-carbonate purification system reduces the CO_2 content of the shifted gas to 0.5 percent and removes essentially all the H_2S and COS . Zinc oxide towers are provided for residual sulfur cleanup.
5. The heating value of the clean gas is increased to 946 Btu by reacting hydrogen with 99.8 percent of the CO in the presence of a nickel catalyst to form methane and water.
6. After gas cooling, the moisture content of the product is reduced to 7 pounds per million standard cubic feet.

The gasifiers are designed to operate at an outlet pressure of 1,160 psig and at maximum temperatures of 1,700° F and 2,700° F for the upper and lower sections, respectively. The thermal efficiency of the plant, using a Western Kentucky No. 11 coal, is 65.3 percent, based on a coal heating value of 13,070 Btu per pound.

Slurry Feeding System

The pulverized coal is mixed with hot condensate to produce a 50-50 weight-percent coal-water slurry and then raised to the system pressure of approximately 1,200 psig with triplex reciprocating pumps. After being preheated to 430° F, the coal slurry is dried in a spray dryer with gasifier product gas that vaporizes the water. The coal and humidified gas at 660° F flow to a cycle separator where the coal drops into a coal hopper and is pneumatically fed to the upper section of the gasifier. This feeding system (3) is illustrated in figure 2. The rest of the integrated plant, (4) shown in figure 3, is the same as described in the lock hopper system except for some changes in the shift conversion, gasification, and heat recovery units owing to shifting of heat loads. The thermal efficiency of the plant is the same as that of the lock hopper system--65.3 percent.

Capital Investment

An economic evaluation was made of an integrated plant sized and designed to produce 250 million scf of high-Btu gas (946 Btu/scf) by two-stage gasification of Western Kentucky No. 11 coal followed by shift conversion, purification, methanation, and pollution control. The total investment is estimated to be \$533.3 million for the lock hopper system, or \$92.4 million higher than for the coal slurry system.

Table 1 is a capital requirement comparison of the two feeding systems. Detailed cost summaries of the major processing units are not included, but the costs of the individual units are listed. General facilities include administrative buildings, shops, warehouses, railroad spurs, rolling stock, roads, waste water treatment, and fences. The costs of steam and power distribution, cooling water towers, plant and instrument air, fire protection, and sanitary water are included in plant utilities.

Operating Cost

Table 2 presents the estimated operating cost comparison for the lock hopper and coal slurry feeding systems. An assumed 90-percent operating factor allows 35 days for downtime, two 10-day shutdowns for equipment inspection and maintenance, and 15 days for unscheduled operational interruptions. With labor at \$6 per hour, payroll overhead at 30 percent of payroll, and depreciation at 5 percent of the subtotal for depreciation, allowing credit for sulfur recovered at \$25 per ton, and with the cost of coal as a variable, the following operating costs are derived:

Cost of coal per ton	Per year, MM		Per MMBtu	
	Lock hopper system	Slurry feeding	Lock hopper system	Slurry feeding
\$11	\$128.0	\$115.8	\$1.64	\$1.48
13	137.1	125.0	1.75	1.60
15	146.3	134.1	1.87	1.72

Based on a 330-day operating year for the plant and allowing credit for sulfur produced, with coal costs and discounted cash flow (DCF) rates as parameters, the average selling prices of the gas per Mscf and per MMBtu for the two systems are shown in the following table:

Coal cost, dollar per ton	Gas selling price											
	Dollars per Mscf						Dollars per MMBtu					
	12-pct DCF		15-pct DCF		20-pct DCF		12-pct DCF		15-pct DCF		20-pct DCF	
	Lock hop- per	Coal slurry	Lock hop- per	Coal slurry	Lock hop- per	Coal slurry	Lock hop- per	Coal slurry	Lock hop- per	Coal slurry	Lock hop- per	Coal slurry
11	2.61	2.28	2.97	2.58	3.64	3.13	2.76	2.41	3.14	2.73	3.85	3.31
13	2.72	2.39	3.08	2.69	3.75	3.24	2.88	2.53	3.26	2.84	3.96	3.42
15	2.83	2.50	3.19	2.80	3.86	3.35	2.99	2.64	3.37	2.96	4.08	3.54

The DCF computer program takes into account the capital expenditure, based on 100-percent equity, prior to startup so that the interest during construction is deleted from the capital requirement. Provisions are made for recovery of the working capital in the 20th year.

Unit Cost Summary

The selling price used to determine the high-cost elements in the process was based on a 15-percent DCF for a 20-year project life, with coal at \$13 per ton. A breakdown of the cost elements for the two systems is shown in table 3.

SUMMARY

As noted in table 1, the lock hopper feeding total investment is \$92.4 million, or 21 percent higher than the slurry feeding system investment. Approximately \$69 million is attributed to difference in feeding systems.

The operating cost of the lock hopper system is about 10 percent higher than that of the slurry feeding system. Increases in maintenance, overhead, and indirect and fixed costs, which are directly related to the capital investment, represent the main difference.

The average selling price was based on three coal costs (\$11, \$13, and \$15 per ton) and three DCF rates of return (12, 15, and 20 percent). Over this range the selling price for the lock hopper system increases from \$0.33 to \$0.51 per Mscf of product, or \$0.35 to \$0.54 per MMBtu. This increase is approximately 15 percent.

CONCLUSION

Results of this study indicate the slurry feeding system is more economical than the lock hopper system, when used to feed a high-pressure (1,200 psig) two-stage gasifier in the Bi-Gas process. It must be kept in mind, however, that this study was conducted under the assumption that the technical problems for both the coal slurry and lock hopper systems have been solved.

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TABLE 1. - Capital requirements, comparison of
lock hopper system with slurry feeding system

Unit	Lock hopper system	Slurry feeding system	Difference
Coal preparation.....	\$14,295,400	\$14,295,400	0
Slurry preparation.....	-	16,435,000	\$+68,743,000
Lock hopper system.....	85,178,000	-	0
Gasification.....	20,698,500	20,698,500	0
Heat recovery No. 1.....	3,402,400	-	+3,402,400
Dust removal.....	2,341,100	2,341,100	0
Shift conversion.....	10,033,200	7,700,000	+2,333,200
Heat recovery No. 2 or 1	8,143,900	23,392,600	-15,248,700
Purification.....	75,713,300	75,281,100	+432,200
Methanation.....	18,782,900	18,782,900	0
Heat recovery No. 3 or 2	21,718,000	21,718,000	0
Drying.....	873,500	873,500	0
Oxygen plant.....	51,975,000	51,975,000	0
Sulfur recovery.....	2,312,500	2,312,500	0
Flue gas processing.....	16,033,300	16,033,300	0
Steam plant.....	22,822,500	20,910,000	+1,912,500
Plant facilities.....	26,574,200	21,956,200	+4,618,000
Plant utilities.....	38,089,700	31,470,500	+6,619,200
Total construction.....	418,987,400	346,175,600	+72,811,800
Initial catalyst requirements.....	2,559,800	2,348,100	+211,700
Total plant cost.....	421,547,200	348,523,700	+73,023,500
Interest during construction.....	63,232,000	52,278,600	+10,953,400
Subtotal for depreciation.....	484,779,200	400,802,300	+83,976,900
Working capital.....	48,477,900	40,080,200	+8,397,700
Total investment...	533,257,100	440,882,500	+92,374,600

TABLE 2. - Annual operating cost,
comparison of lock hopper system with slurry feeding system

Cost item	Lock hopper system	Slurry feeding system	Difference
Direct cost:			
Raw materials:			
Coal at \$11/ton.....	\$50,294,400	\$50,294,400	0
Raw water.....	1,176,100	1,211,800	\$-35,700
Catalyst and chemicals.	2,517,300	2,504,200	+13,100
Methane.....	455,600	455,600	0
Subtotal.....	54,443,400	54,466,000	-22,600
Direct labor.....	2,470,300	2,522,900	-52,600
Direct labor supervision..	370,500	378,400	-7,900
Subtotal.....	2,840,800	2,901,300	-60,500
Maintenance labor.....	7,815,000	6,465,000	+1,350,000
Maintenance supervision..	1,563,000	1,293,000	+270,000
Maintenance material and contracts.....	11,722,500	9,697,500	+2,025,000
Subtotal.....	21,100,500	17,455,500	+3,645,000
Payroll overhead.....	3,665,600	3,197,800	+467,800
Operating supplies.....	4,220,100	3,491,100	+729,000
Total direct cost.	86,270,400	81,511,700	+4,758,700
Indirect cost.....	11,264,600	9,539,200	+1,725,400
Fixed cost:			
Taxes and insurance.....	8,430,900	6,970,500	+1,460,400
Depreciation.....	24,238,900	20,040,100	+4,198,800
Total, before credit.	130,204,800	118,061,500	+12,143,300
Sulfur credit.....	2,226,700	2,226,700	0
Operating cost, after credit	127,978,100	115,834,800	+12,143,300

TABLE 3. - Unit cost comparison

Process unit	Cost per Mscf of product	
	Lock hopper system	Slurry feeding system
Coal preparation	\$0.13	\$0.13
Gasification	1.32	1.41
Lock hopper system50	-
Slurry preparation.....	-	.16
Dust removal02	.02
Shift conversion18	.05
Purification64	.63
Methanation17	.17
Drying01	.01
Sulfur recovery	-	-
Flue gas processing11	.11
Total	3.08	2.69

Basis: Coal at \$13/ton - 15% DCF.

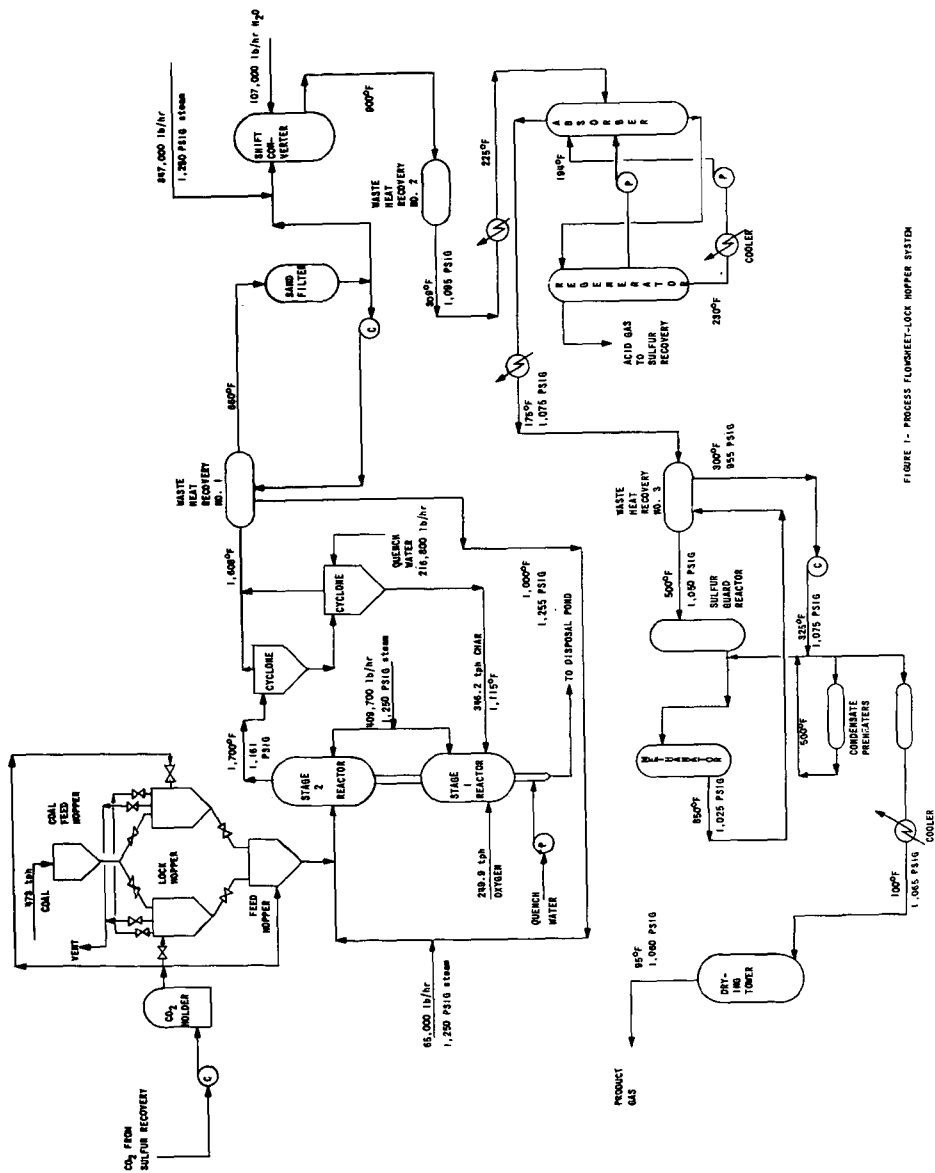


FIGURE 1- PROCESS FLOW-SHEET-LOCK HOPPER SYSTEM

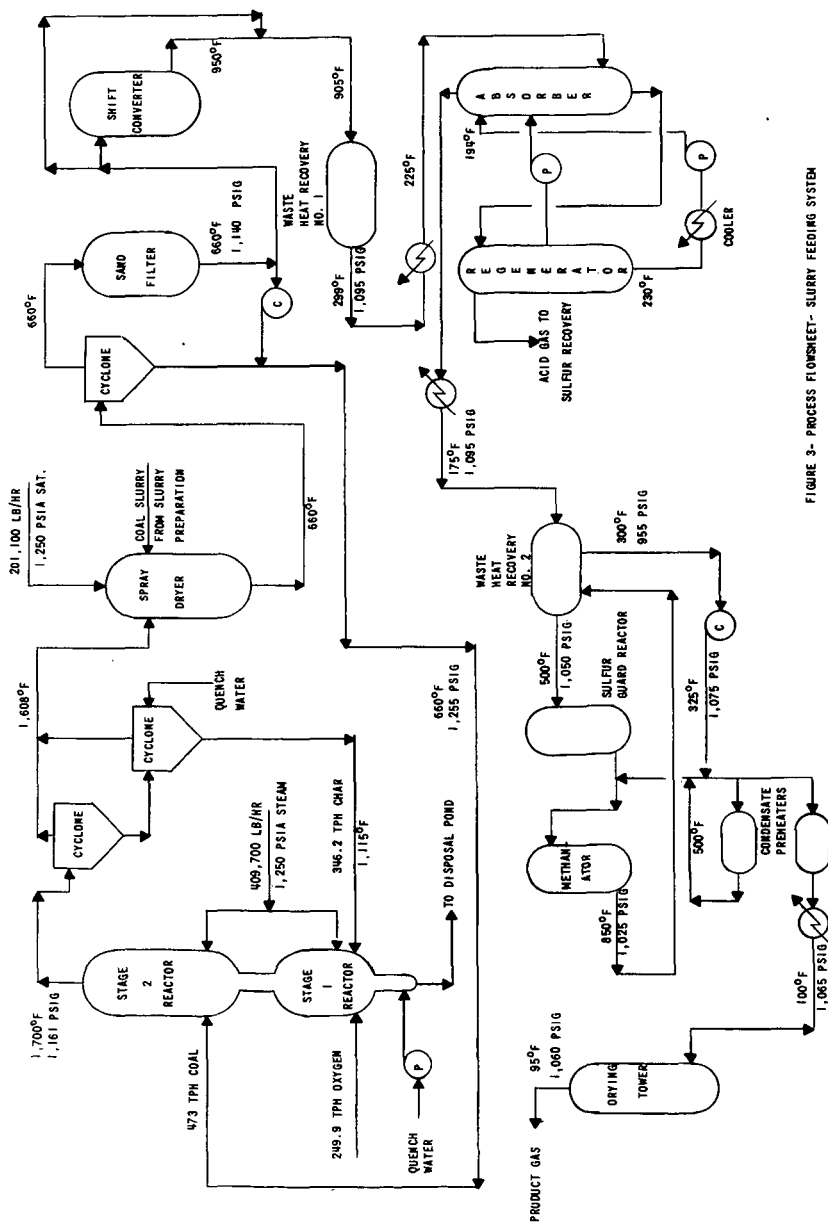


FIGURE 3- PROCESS FLOWSHEET- SLURRY FEEDING SYSTEM

Coal Desulfurization During Gaseous Treatment

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Sulfur removal from coal during treatment in gaseous atmospheres at elevated temperatures is of interest both because such a treatment might serve as a basis for a coal desulfurization process and because knowledge of the fate of sulfur under such conditions has application to the behavior of coal during carbonization or gasification. In the work reported here, desulfurization of both a raw and deashed Iowa coal were investigated in three different gases, nitrogen, hydrogen and a 6% oxygen-94% nitrogen gas mixture. With each gas, both the temperature and holding time at temperature were varied. With hydrogen and nitrogen, the temperature was varied between 300 and 700°C. The temperature range used with the oxygen-nitrogen mixture was only from 350 to 455°C due to the large weight loss at higher temperatures caused by combustion of the sample. Holding time at temperature was varied from 0 to 60 min.

EXPERIMENTAL

The investigation was carried out in a Rigaku CN8001 H type thermal analyzer which included a thermal gravimetric analyzer, a preprogrammed heating unit and temperature control system, and a data recording unit. To carry out a run, about 300mg of coal (<125 μ) was placed on the sample pan of the thermal analyzer and heated to the desired temperature using a heating rate of 20°C/min while maintaining a flow of gas over the sample. After holding the sample at temperature for the desired period of time, the gas flow was switched to nitrogen and the reaction chamber was cooled with the initial cooling rate being on the order of 250°C/min. The sample weight was recorded continuously, and at the end of the run the total and organic sulfur contents of the treated coal were determined.

The coal came from the Jude mine, Mahaska County, Iowa, and is a high-volatile-C bituminous coal. The raw coal contained 3.25% inorganic sulfur and 3.04% organic sulfur (moisture-free basis). The deashed Jude coal was prepared by twice floating the raw coal in a heavy liquid medium having a specific gravity of 1.3. It contained 4.74% organic sulfur, but only 0.69% inorganic sulfur. Thus, the results of experiments using the deashed coal manifested largely the behavior of the organic sulfur compounds in the coal. The analyses of the raw and deashed coal are shown in Table 1.

Table 1. Proximate analyses of coal samples

Proximate Analysis	Raw Coal	Deashed Coal
Moisture	1.22%	2.21%
Ash	18.80%	5.54%
Volatile matter	39.68%	45.72%
Fixed carbon	40.30%	46.53%

*Currently at Allis-Chalmers, Milwaukee, Wisconsin.

RESULTS AND DISCUSSION

Effect of Temperature and Holding Time

The effect of temperature upon sulfur removal in each of the three gases was investigated by heating the coal sample to the desired temperature using a heating rate of 20°C/min. followed by immediate cooling. In nitrogen, the amount of sulfur in all forms except for the organic sulfur in the raw coal tended to decrease with increasing temperature, with the decrease being greater for the deashed coal. At 700°C, the total sulfur content of the raw coal and the total and organic contents of the deashed coal were 5.60, 3.27 and 3.05 wt.%, respectively. On the other hand, the organic sulfur content of the raw coal increased from 3.04 to 4.82 wt.% as the temperature was increased from room temperature to 700°C. Since the raw coal contained a substantial amount of inorganic sulfur, this result indicated that inorganic sulfur was being transformed into organic sulfur during the heating process.

The various sulfur contents of the coal samples were not greatly affected when the coal was held at constant temperature. At lower temperatures, the sulfur contents tended to decrease slightly, while they tended to increase when held at higher temperatures.

Fig. 1 shows the effect of temperature on the total and organic sulfur content of the raw and deashed coal when treated with hydrogen. Again, except for the organic sulfur content of the raw coal which increased slightly, the various sulfur contents all decreased with increasing temperature. When the coal was held at temperature for extended periods, there was little change in the sulfur content at temperatures below 600°C. However, at higher temperatures the sulfur content decreased significantly when the sample was held at temperature in hydrogen.

The effectiveness of hydrogen for preferential removal of the organic sulfur can be determined by comparing the differences in the amount of organic sulfur removed during treatment with nitrogen and hydrogen. Any desulfurization in nitrogen is due to the evolution of volatile compounds containing sulfur. Therefore, no matter what the temperature or treatment time, a unique relationship should exist between the organic sulfur removed and the weight loss. The data collected with deashed Jude coal did indeed exhibit such a relationship (Fig. 2).

In hydrogen, sulfur is removed either by devolatilization, as in nitrogen, or by reaction of the hydrogen with sulfur in the organic matrix to form hydrogen sulfide. The effectiveness of hydrogenation for desulfurization can be judged by comparing the organic sulfur removed versus weight loss curves in hydrogen and nitrogen (Fig. 2). Up to a weight loss of about 40% (point A, Fig. 2), the organic sulfur loss curves in the two gases were nearly the same. However, at higher weight losses, the organic sulfur removed in hydrogen increased rapidly with only a slight increase in weight loss indicating that the sulfur-hydrogen reaction was taking place. All the experimental points at weight losses greater than that shown by point A were taken at 600 and 700°C. Reaction of hydrogen with the sulfur in coal appears therefore to be significant only at temperatures above 600°C. At lower temperatures, desulfurization in both hydrogen and nitrogen occur only due to removal of volatile, sulfur-containing compounds. The onset of the hydrogen-sulfur reaction accounts for the reduction of sulfur content with increased holding time at temperatures above 600°C.

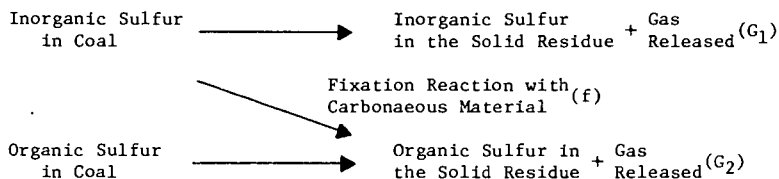
The final gas tested was a mixture of nitrogen with 6% oxygen. The effect on the sulfur content of treatment in the range from 350 to 455°C was slight, with a small decrease in the amount of all forms of sulfur occurring if the coal was held at a temperature in this range. However, the amount of sulfur in the coal decreased fairly substantially as the coal was heated from room temperature to

350°C in an oxidizing atmosphere with the sulfur contents of the two coals at 350°C being as follows:

	Sulfur Content, wt. %	
	Total	Organic
Raw coal	4.77	2.58
Deashed coal	3.87	3.39

Transformation of Sulfur

As previously noted, the results of the experiments indicated that some of the inorganic sulfur was trapped by the organic portion of the coal during the heating process. This same phenomenon has been observed by Snow (1) and Cernic-Simic (2). In an attempt to estimate the fraction of inorganic sulfur released as gas (G_1) or transformed into organic sulfur (f) and the fraction of original organic sulfur released as gas (G_2), the following reaction scheme was postulated.



By assuming that this scheme applied to both the raw and deashed coal, G_1 , G_2 and f were estimated from sulfur material balances. Details of the calculations are available elsewhere (3).

The fixation reaction, characterized by f , started at 300°C in nitrogen and increased rapidly between 400 and 500°C with f reaching 0.7 at 700°C. G_1 was generally small at all temperatures, being between 0 and 0.1. G_2 increased rapidly between 300 and 500°C, and then started to level off between 600 and 700°C. About 70% of the original organic sulfur was released as gaseous compounds at 700°C. In nitrogen, the effect on G_1 , G_2 and f of holding time when the sample was kept at constant temperature was small.

The fraction of inorganic sulfur transformed into organic sulfur (f) was larger in hydrogen than in nitrogen at low temperatures (Fig. 3). However, f remained constant at temperatures above 400°C. G_1 was again small, while G_2 increased with increasing temperature as it had in nitrogen. f and G_2 increased slowly when the samples were held at 400°C, while G_1 remained relatively constant. At 700°C, G_1 and G_2 both increased slightly with holding time, but f decreased from 0.5 to about 0.2 when the holding time was varied from 0 to 60 min. Apparently the H_2S formed from the organic sulfur reacted with the iron to produce FeS .

The fraction of inorganic sulfur transformed into organic sulfur (f) in the oxidizing atmosphere was comparable to that in nitrogen at the same temperature. It increased rapidly from about 0.1 at 350°C to 0.36 at 450°C. The fraction of inorganic sulfur released into the gas phase (G_1) was much larger than in nitrogen or hydrogen since the reaction of pyrite with oxygen is thermodynamically more favorable than the reaction of pyrite with hydrogen. G_1 was almost unchanged with temperature between 350 and 455°C and was equal to about 0.3. G_2 also was larger in the oxygen-nitrogen mixture and increased rapidly with temperature. About 55% of the organic sulfur was released at 455°C. G_1 and G_2 both increased with holding time at 400°C in the oxidizing atmosphere, while f decreased as the holding time was increased.

CONCLUSIONS

Temperature is the most important factor influencing desulfurization in the three gases tested. The holding time at temperature is less important except in the case of hydrogen above 600°C where the sulfur content of the sample decreases with increased holding time. The experimental evidence indicated that this was due to the direct reaction of hydrogen with sulfur in the organic portion of the coal which takes place only at temperatures of 600°C or above. It was observed in the experiments that some inorganic sulfur was transformed into organic sulfur during the gaseous treatment. The fractions of inorganic and organic sulfur released as gases and the fraction of inorganic sulfur transformed into organic sulfur were estimated for each of the gas atmospheres and conditions of temperature and time used.

Acknowledgement

Funds for this research were provided by the Iowa Coal Project with money made available by an appropriation from the Iowa Legislature in June 1974.

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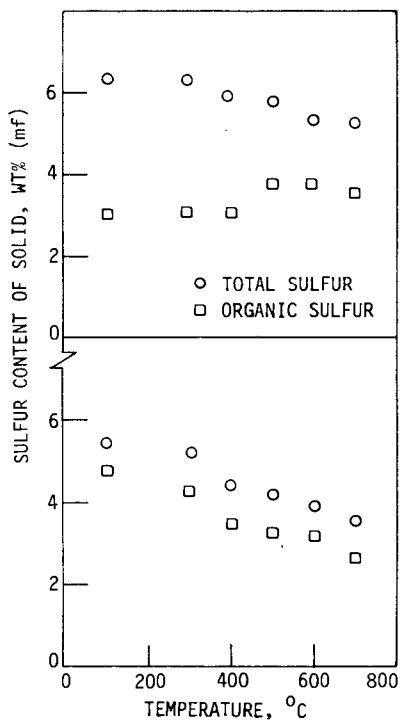


Fig. 1. Effect of temperature on the sulfur content of raw* and deashed coal heated in hydrogen.

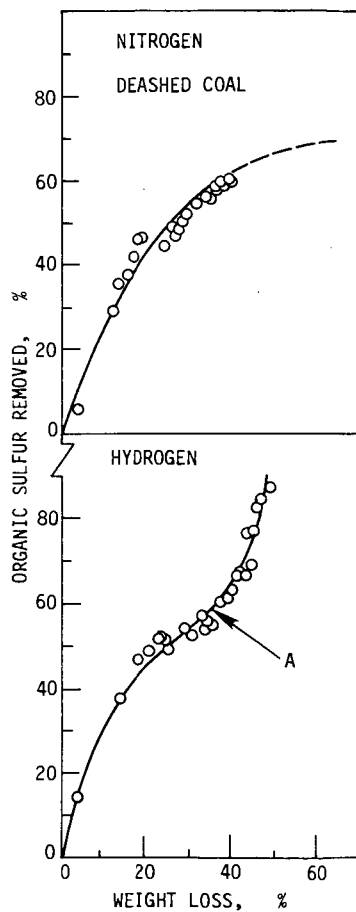


Fig. 2. Organic sulfur removal as a function of sample weight loss for deashed coal.

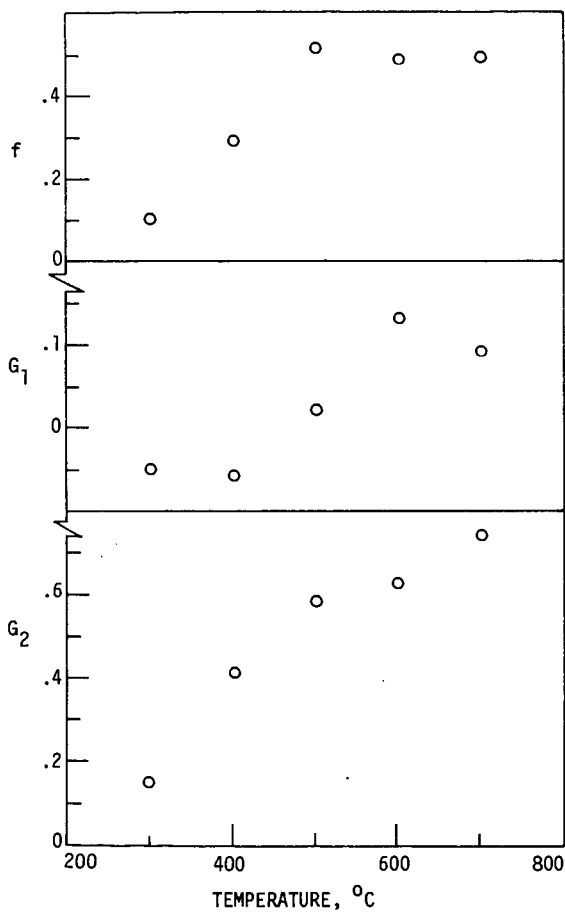


Fig. 3. Effect of temperature on the transformation of sulfur in a hydrogen atmosphere.